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16. ABSTRACT

A pilot plant was designed and constructed to produce char via the St. Regis hydropyrolysis kraft chemical recovery process and to produce activated carbon from the char. This report includes discussion of laboratory and prepilot work, the pilot plant, and presents operating results.

After a period of optimizing feed pretreatment, temperature and pressure conditions in the hydropyrolysis section of the plant, about 22,000 kg of char was produced for activation. The char was converted to a high quality granular activated carbon having properties which compared favorably with commercially available carbons. The concept of on-site production of activated carbon and the use of such carbon for local effluent treatment has been demonstrated to be technically sound.

The cost of on-site production of hydropyrolysis activated carbon in quantities required for local effluent treatment is not competitive with commercially available carbons. To become competitive, the plant would have to supply carbon for effluent treatment at several locations. To achieve significantly lower costs would require entry into market production.

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ON-SITE PRODUCTION OF ACTIVATED CARBON FROM KRAFT BLACK LIQUOR

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FOREWORD

When energy and material resources are extracted, processed, converted, and used, the related pollutional impacts on our environment and even on our health often require that new and increasingly more efficient pollution control methods be used. The Industrial Environmental Research Laboratory-Cincinnati (IERL-Ci) assists in developing and demonstrating new and improved methodologies that will meet these needs both efficiently and economically.

This report presents the findings of a pilot-scale project on the production of char and activated carbon from kraft black liquor. The granular activated carbon compared favorably to commercial activated carbons in its ability to treat kraft mill wastewater. The results will interest both industry and regulatory agencies in considering alternatives for effluent polishing and color removal. Cost estimates are also presented. For further information contact the Food and Wood Products Branch, Industrial Environmental Research Laboratory - Cincinnati.

David G. Stephan
Director
Industrial Environmental Research Laboratory
Cincinnati

ABSTRACT

The overall objective of this grant program was to develop and demonstrate an economical system for producing a reusable water from kraft pulp and paper mill effluent. The objective of Part II of the program was to demonstrate the production and activation of a carbon char derived from black liquor and develop the economics of on-site production of activated carbon.

A pilot plant was designed and constructed to produce char via the St. Regis hydropyrolysis kraft chemical recovery process and to produce activated carbon from the char. This report includes discussion of laboratory and prepilot work conducted outside the grant program which formed the basis for pilot plant design. The report describes the plant and presents operating results.

After a period of optimizing feed pretreatment, temperature, and pressure conditions in the hydropyrolysis section of the plant, about 22,000 kg of char was produced for activation. The char was converted to a high quality granular activated carbon having properties which compared favorably with commercially available carbons. The concept of on-site production of activated carbon and the use of such carbon for local effluent treatment has been demonstrated to be technically sound.

The cost of on-site production of hydropyrolysis activated carbon in quantities required for local effluent treatment is not competitive with commercially available carbons. To become competitive, the plant would have to supply carbon for effluent treatment at several locations. To achieve significantly lower cost would require entry into market production.

This report was submitted in fulfillment to Grant No. 12040 EJU under the partial sponsorship of the U. S. Environmental Protection Agency. This report covers the period from November 1, 1971 to September 30, 1975 and work was completed as of September 30, 1975.

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Sadly, but gratefully, the authors acknowledge the genius of the late Mr. W. G. Timpe who invented the hydropyrolysis process, developed the concepts which led to this grant program, and organized the execution of the program.

SECTION I

INTRODUCTION

St. Regis Paper Company, with partial support by EPA, initiated a program in July, 1969, to develop and demonstrate an economical system for producing a reusable water from kraft pulp and paper industry effluent. The program was organized in two parts. Part I covered the use of activated carbon in effluent treatment and the pilot plant demonstration was completed in December, 1972. The objective of Part II as proposed orginally was to demonstrate the production and activation of a carbon char produced from black liquor and determine the economics of the mill site preparation of the activated carbon.

Two reports have been issued. The first report (1) was a survey of the literature and a review of industry information on effluent treatment and the reuse of treated water in pulp and paper mills. The second report (2) described laboratory investigations and the design, construction and operation of the pilot plant utilizing activated carbon, alone and in sequence with other treatment steps, to treat the combined effluent streams from an unbleached kraft pulp and paper operation. Capital and operating cost estimates were included in the report.

It was concluded from Part I of the program that treatment sequences involving carbon adsorption can produce reusable water having a remaining color of 100 APHA-NCASI color units (CU) and a remaining total organic carbon (TOC) of 100 mg/l. Based on the survey of the literature and industry information, these had been defined as the tentative criteria for a reusable general process water. Treatment for reuse was confirmed as an attractive alternative to treatment for discharge, particularly in the light of expected future discharge standards.

It was recommended that a better working definition of reusable water be established and that grants be initiated to demonstrate actual reuse of treated effluents on a mill scale. The results of such work could significantly alter the definition of reusable water and change the relative economics of treatment for reuse versus treatment for discharge. This work was not within the scope of the St. Regis program.

Assuming that activated carbon would have application in the production of reusable water, the original grant proposal had anticipated that the cost of carbon would have a significant impact on the economics of treatment. The results of Part I showed this to be true in varying degrees depending on

the treatment sequence. Part II of the grant proposal had suggested that activated carbon produced on-site from material available on-site would be lower in cost than activated carbon obtained through normal commercial channels. Specifically, it was proposed that activated carbon be produced from kraft black liquor as a by product of hydropyrolysis recovery of kraft pulping chemicals.

On-site production and use of activated carbon was expected to show savings in raw material acquisition and shipping costs, savings through integration of energy inputs and outputs with the hydropyrolysis process, and savings in packaging and shipping of the activated carbon.

The hydropyrolysis process was conceived and partially developed by St. Regis prior to the July, 1969, EPA grant. The patent application and detailed data were submitted to EPA and placed in background. St. Regis agreed to future licensing of the hydropyrolysis process to those who might wish to utilize the process as a starting point for on-site production of activated carbon.

This report describes successful pilot-scale production and activation of hydropyrolysis char and develops the economics of on-site production of activated carbon.

SECTION II

CONCLUSIONS

1. A char suitable for production of activated carbon can be obtained via the hydropyrolysis kraft chemical recovery process. Char production has been demonstrated in a pilot plant system.

2. Hydropyrolysis reaction conditions must be selected and controlled to produce acceptable char while avoiding operational problems. A range of satisfactory operating conditions has been defined.

3. Production of granular activated carbon from hydropyrolysis char has been demonstrated in a pilot plant system.

4. Hydropyrolysis char is a good starting material for production of granular activated carbon. The char can be compacted using little or no added binder material. Activation rates are high.

5. Hydropyrolysis char requires calcining before activation.

6. Hydropyrolysis activated carbon has properties - surface area, hardness, adsorption performance - which compare favorably with commercially available carbons.

7. Pilot plant experience and operating data provide a sound basis for commercial plant design and cost estimates.

8. The cost of on-site production of hydropyrolysis activated carbon in quantities required for local effluent treatment is estimated to be $1.52/kg (October 1975 dollars). This cost is not competitive with commercially available carbons at $0.88 - $1.10/kg.

9. The production cost of hydropyrolysis activated carbon decreases as the production level increases. To become competitive, the plant would have to supply carbon for effluent treatment at several locations. To achieve significantly lower costs would require entry into market production.

10. On site production of activated carbon has an effect on the cost of effluent treatment, primarily through the carbon regeneration cost element. Treatment costs become significantly lower if the activated carbon plant is servicing three or more treatment plants.

SECTION III

RECOMMENDATION

The concept of on-site production of activated carbon, using readily available on-site materials (black liquor), and the use of such carbon for local effluent treatment has been demonstrated to be technically sound. No further work nor application of this technology is recommended at this time because current economics do not favor this approach to effluent treatment. There may be specific instances in which the economics would be more favorable. Also, changing economics conditions could alter this recommendation in the future.

SECTION IV

HYDROPYROLYSIS PROCESS DEVELOPMENT PRIOR TO PILOT PLANT DESIGN

The desire to eliminate the problems associated with the conventional kraft recovery system and the potential for economically more attractive recovery processes prompted St. Regis to undertake a research and development program in this area. The economical recovery of new organic chemicals or other byproducts (for example, activated carbon) would be a long range objective. Several new processes were developed and pursued by St. Regis with the hydropyrolysis process resulting as the most attractive for kraft recovery. Hydropyrolysis is a process for the recovery of pulping chemicals and energy from kraft black liquor. The process has been described in a US Patent (3).

In the hydropyrolysis process, kraft black liquor is subjected to high temperature while being maintained under pressure in the liquid state. Under these conditions, the organic components of the black liquor are converted to a carbonaceous solid (char) which is dispersed as a slurry in the aqueous phase. This reaction of the organics also generates a gaseous phase which separates from the aqueous slurry when pressure is reduced at the discharge end of the reaction system. The gaseous product can be burned to generate heat for input to the hydropyrolysis reaction system and the sulfur values in the gaseous product can be recycled to the feed black liquor.

Most of the sulfur and essentially all of the sodium in the black liquor are retained in the liquid phase of the product slurry. Small fractions of the sodium and sulfur are found in the char. After filtration and washing, the char is suitable for combustion as a relatively clean fuel or for thermal treatment to produce activated carbon. The filtrate essentially has the composition of green liquor and is reacted with lime (CaO) to regenerate kraft pulping chemicals.

During the period 1969-1972 St. Regis conducted an intensive laboratory research program using batch reactors to examine reaction variables: temperature, time, feed liquor concentration, and effect of recycled gaseous components. Fundamental experiments were carried out to determine heat transfer data for black liquor in a temperature and pressure range well above anything reported in the literature, with attention given to the influence of a disperded solid phase and a gaseous phase.

Based on the results, a prepilot reactor system was designed and constructed. Operation of the prepilot system yielded the data and operating experience needed before the pilot plant design phase could be initiated. Timpe and Evers (4) have summarized the work completed during the 1969-1972 period, so there is no need to describe the results in any detail.

The results of the laboratory research program and operation of the prepilot system identified the process flowsheet as that shown in Figure 1. In this figure, the hydropyrolysis process is divided into unit processes or operations, which are the following:

1) Pretreatment
2) Pressurization
3) Heat recovery
4) Heating and reaction
5) Pressure letdown
6) Flash gas separation
7) Flash gas combustion and recycle
8) Liquid-solid separation and char washing

Black liquor, after three effects of evaporation and soap skimming, contains 25% solids, and is fed to the process. Before the black liquor can be pressurized or reacted, it must be subjected to a pretreatment which involves the absorption of SO_2 into the liquor. After pretreatment, the treated black liquor is pressurized by pumping and heated to a reaction temperature at which char formation proceeds with a reasonable rate. The heating process occurs in two steps. First, the treated black liquor is heated by the hot slurry stream leaving the reactor in a heat recovery process, then the liquor is heated to reaction temperature by a process which utilizes an outside source of energy. After heating, the liquor enters the reactor where the char formation reaction occurs. After leaving the reactor, the slurry is cooled in the heat recovery unit and flashed by a pressure reduction process. The flash gas is separated from the slurry, combused, and recycled to black liquor pretreatment. The char in the slurry from flash gas separation is separated from the liquor and the char is washed to recover entrained pulping chemicals. The liquor and concentrated wash contain the inorganic pulping chemicals; these are combined and sent to the caustic plant. The washed char, after drying, can be used as a boiler fuel or further processed into activated carbon.

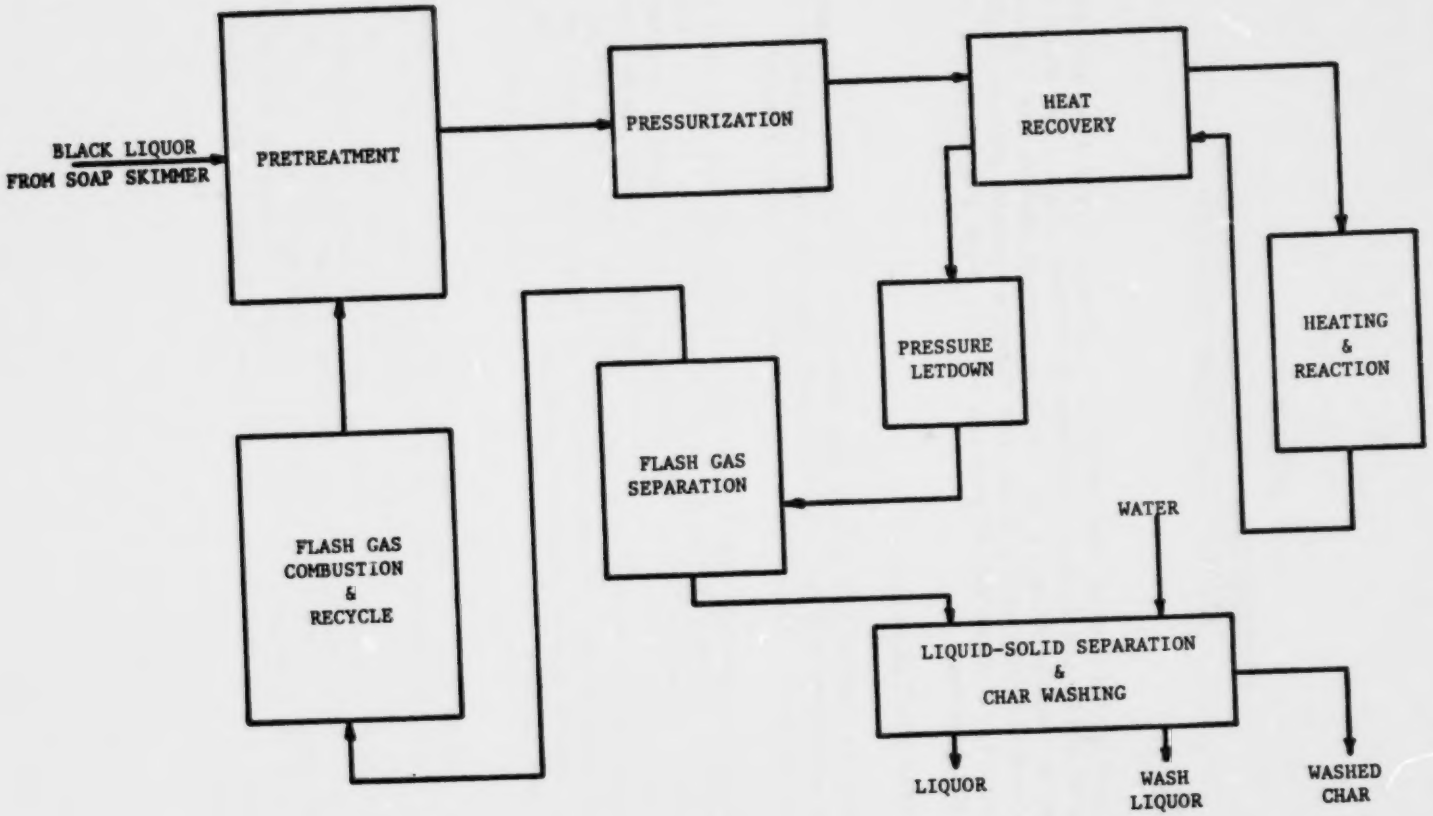


Figure 1. Flow diagram for the hydropyrolysis process

SECTION V

ACTIVATED CARBON TECHNOLOGY DEVELOPMENT PRIOR TO PILOT PLANT OPERATIONS

INTRODUCTION

This section discusses the nature of hydropyrolysis char and laboratory production of activated carbon from hydropyrolysis char. The section also covers work on regeneration of St. Regis activated carbon and a series of tests to correlate laboratory fluid bed furnace results with multiple hearth furnace results. A substantial protion of this work was conducted outside the EPA grant program.

NATURE OF HYDROPYROLYSIS CHAR

In order to understand better the mechanism by which a carbonaceous material is activated and to interpret data taken during activation runs, it is necessary to have a knowledge about the material being treated.

The organic compounds present in black liquor are the modified lignins and carbohydrates present in wood. Artificial coalification (5) studies have shown that coal-like bodies are produced by hydrothermal treatment of lignin and cellulosic substances. These studies also have shown that an alkaline medium favors the production of substances with weak coking properties. Therefore, the carbonaceous product from hydropyrolysis of kraft black liquor should have a structure similiar to low rank coals. It is well known that good quality activated carbons are produced commercially from coals (6).

Torikai and Walker (7) have reviewed the literature on activation of coals. They find that relatively high volatile coals, from 14% to 38% volatile matter, have been activated by various investigators to produce excellent activated carbons. Conditions of preliminary carbonization and activation are widely varied. King, MacDougall, and Gilmour (8) have reported that the best starting materials contain about 38% volatile matter, 82% carbon, and 5% hydrogen. Torikai and Walker (7) show an analysis of two bituminous coal lithotypes which were reacted to produce satisfactory activated carbons.

	Proximate Analysis, %					Ultimate Analysis, %		
	Moisture	Ash	Volatile matter	Fixed carbon	Sulfur	Carbon	Hydrogen	Nitrogen
Coal A	2.1	3.9	37.6	62.4	0.63	85.0	5.6	1.4
Coal B	2.5	2.1	38.3	61.7	0.88	83.4	5.8	1.6

In order to determine the nature of hydropyrolysis char and compare it to coals, several analyses were carried out. Among these were analyses for carbon and hydrogen. Char A was washed and dryed and Char B was the same material after a carbonizing step.

	Carbon %	Hydrogen %
Char A	84.53	3.23
Char B	86.18	3.18

Comparing the values of Char A with the data for bituminous coals, it is shown that hydropyrolysis char contains nearly the same weight of carbon as the coals reported: 84.53% as opposed to 84.2% average for two coals. When hydrogen content is compared, however, it is seen that the hydropyrolysis char has significantly less hydrogen than the coals: 3.23% for char that has not been thermally treated vs. 5.7% average for coals. The mole ratio of hydrogen to carbon is also less: 0.458 for the untreated char as opposed to 0.80 for the coals. Several tests showed volatile matter to vary between 30 and 40% for experimental char. Comparing this with the values for coals, we see that the hydropyrolysis chars are quite similar to coals in volatile content.

Since certain metals present in carbonaceous materials have been reported to act as catalysts in some gasification reactions, Char A was analyzed for metal ions. The results, calculated as % in the ash, are shown below. Also included are values for the ash content of Pennsylvania bituminous coals.

Element	Hydropyrolysis char	Pennsylvania bituminous coal[a]
Sulfur	-	2.4
Sodium	10.0	0-2.6
Iron	11.0	4.5
Calcium	4.0	7.2
Magnesium	2.0	1.1
Chromium	6.0	-
Nickel	2.0	-
Silicon	-	55.5
Aluminum	-	17.0
Titanium	-	1.7
Potassium	-	0-3.0
Total Ash	2.4	3-8

[a]Perry's Chemical Engineers Handbook, Fourth Edition.

These data show that hydropyrolysis char, as a raw material for activated carbon, ranks on the low side in total ash when compared to bituminous coals, but that this ash is composed of different elements in different amounts. How this different composition should effect the gasification or activation of char was not certain at this time.

CARBONIZATION

It is generally known that, in order for a material to be a candidate for activated carbon manufacture, it must be carbonaceous, stable to mild oxidation, have a relatively low ash content, and also contain some internal pore structure. The reason for such a structure is to provide the activating gas with a means of entering the carbon particle, to react with it, and then return to the surroundings as a reaction product. In this manner, micropores are enlarged, new pores previously unavailable to activating gases are opened, and the result in development of the surface area necessary for adsorption. The access to the micropores described above is quite often through macropores that exist naturally in the surface of carbonaceous materials. The absence of such macropores does not mean that micropores are not present, but in their absence the development of micropores can be greatly inhibited. When macropores are not naturally present, they sometimes can be produced by a heat treatment step (calcination) prior to activation.

It has been shown that hydropyrolysis char has many of the properties of coal. It is known (9) that when coals are heated from ambient temperature to temperatures above 400°C , they undergo a transition, similar to the glass transition in polymers, in the temperature range between 300 and 400°C. At the same time, a considerable amount of volatile matter escapes. On heat treatment, a portion of the material melts. During this time, the material undergoes active decomposition with the elimination of smaller molecules and formation of carbon-carbon bonds. Thus, escape of volatiles through the liquid phase creates a porous structure and the carbon-carbon bond formation which takes place at a higher temperature tends to make the system rigid, thus retaining the porous structure. Upon further heating, the carbon-carbon bond formation continues and blocks out some pores already formed.

Early attempts to activate hydropyrolysis char were unsuccessful, perhaps owing to the omission of a carbonizing step to develop a macropore structure. From this it was hypothesized that the carbonization step developed the necessary macropore structure for successful activation.

Torikai and Walker (7) have suggested a method by which the presence or absence of an internal pore structure can be detected and evaluated relative to materials known to produce high quality activated carbons. The BET nitrogen surface area of porous solids is obtained by measuring the adsorption of nitrogen at 77°K (10). Experience with porous carbons has shown that nitrogen is essentially excluded from pores less than about 5.5Å in diameter under the conditions of measurement (11). Carbon dioxide surface area, on the other hand, is measured at 298°K (12). The carbon dioxide molecule can enter into pores of about 3.0 Å. Thus, the carbon dioxide surface area is believed to include all pores above 3.0 Å in diameter. It should be realized that this approach gives strictly a measure of micropore volume which is then converted to an equivalent surface area. Both the BET nitrogen method and the carbon dioxide Dubinin method have certain theoretical limitations. These limitations however, are of little concern in evaluating the effectiveness of a micropore structure. It is the magnitude of the difference between the two values that reflects the presence of pores in the range of 3.0 Å to 5.5 Å. The larger the difference between the two areas, the greater is the probability that a satisfactory pore structure exists.

Initial studies of the carbonization of hydropyrolysis char were carried out to see if a micropore structure could be developed suitable for subsequent activation. Hydropyrolysis chars and some coals were analyzed for their nitrogen and carbon dioxide surface areas.

Sample	Sample treatment	(A) N_2 area m^2/g	(B) CO_2 area m^2/g	(B)-(A)
Coal A[1]	None	88.4	169	80.6
Coal A[1]	Carbonized	77.4	612	534.6
Coal B[1]	None	32.0	148	116.0
Coal B[1]	Carbonized	19.1	456	436.9
Hydropyrolysis Char	None	0.6	128	127.4
Hydropyrolysis Char	Carbonized	36.0	445	409.0

1 Soft coals of the lignite variety.

There are several points of interest in this analysis, Hydropyrolysis char had nitrogen and carbon dioxide surface areas of 0.6 and 128 m^2/g, respectively, before any heat treatment. This showed that the material already had micropore area in the range of 3.0 to 5.5Å in diameter. This inherent pore structure should be advantageous for subsequent activation. Upon thermally treating this char, the two areas were enlarged to 36.0 and 445.0 m^2/g, respectively, interpreted to mean a substantial increase in micropore area had been achieved and a number of micropores had been created by the mechanism previously discussed.

As shown then, hydropyrolysis char after carbonization compares favorably with selected coals in terms of the necessary pore structure for activation, as measured by comparing nitrogen and carbon dioxide surface areas.

The difference of 409 m^2/g in these areas is considered very satisfactory for the material to have potential for activation. In fact, differences in carbon dioxide and nitrogen areas up to 592 m^2/g have been attained which exceeds the values for the coals.

ACTIVATION

As mentioned previously, the properties of activated carbons depend on the existence within the carbon particle of an extensive micropore structure. Gasification by steam or carbon dioxide is the principal method used to modify this microporosity. It has been shown by Marsh and Rand (13) that the development of porosity is a combination of two processes: the widening of existing pores and the opening of closed pores. The process of pore widening has been demonstrated by Kipling and McEnany (14).

Although initial attempts to activate hydropyrolysis char met with limited success, the results firmly established the fact that the char could be activated, and provided an indication of the reactivity of the material.

The original laboratory activation apparatus, a fixed bed design, had the serious experimental limitation of non-uniform exposure of the carbon particles to the activating gas. This led to the development of a fluidized bed reactor system. It was in this apparatus that all future activations would be accomplished until pilot plant startup.

Activation studies in the fluidized bed reactor included the use of carbon dioxide with nitrogen, water vapor with nitrogen, and flue gas. Flue gas, as used in this discussion, refers to the products of the stoichiometric combustion of methane with air giving a product (activating) gas of the composition: 72.7% N_2,
18.2% H_2O, and
9.1% CO_2.

It must be noted that, although these runs produced a granular carbon, the particle strength was far below commercial acceptability. The products should be considered as powdered carbons. Later in the project, the decision was made to produce a true granular carbon.

To simplify equipment operation and data analysis, the first activations utilized carbon dioxide gas with nitrogen. Fractional weight loss as a function of time for various CO_2 concentrations and temperatures of 750°C and 850°C, was found to be linear and suggests a rate which is zero order with respect to the carbon. Differences in results for the different gas concentrations indicate that the rate is dependent on gas concentration.

Surface areas above 1200 m^2/g were attained. Surface areas for commercial carbons fall in the range of 550-1000 m^2/g. To achieve these areas, hydropyrolysis char would have to be reacted to 50% weight loss with CO_2 as the activating gas. At higher CO_2 concentrations, this weight loss was attained in 60-80 minutes.

In addition to CO_2 and N_2, flue gas contains water vapor. Weight loss data during the activation of char with water vapor were obtained. The rate at all water vapor concentration levels is linear and independent of the carbon present. A rate dependency on the water vapor concentration is similar in trend to that of CO_2 at 850°C. For activation with water vapor at 850°C, the development of total N_2 surface area showed a maximum surface area in the range of 40-60% weight loss. This weight loss occurred after 40-80 minutes at water vapor concentrations above 20%. Surface areas from 700 to over 1000 m^2/g were obtained in this range of weight loss.

The limited amount of data obtained for flue gas activations at 750°C and 850°C indicated that the rate is approximately the sum of the rates

for the individual gases. Thus, each reaction appears to proceed independently. Relating these data to values for coal reactivity showed that hydropyrolysis char in general is more reactive than coal.

All of the above observations point to the fact that kraft hydropyrolysis char is a good material for activated carbon production. Data taken on carbons produced from this material have shown nitrogen surface areas and open pore volumes that compare exceptionally well with commercially available carbons.

REGENERATION OF ST. REGIS ACTIVATED CARBONS

Granular carbon is utilized generally in packed beds. The liquid or gas stream to be treated is forced downward or upward through the beds. In this manner, each successive layer of carbon in a given bed acts to remove impurities, with maximum adsorption taking place in the early stages of contact, and less and less taking place as the gradually purified solution continues on. Ultimately, the carbon becomes loaded to the point where the product stream exceeds specifications. The economics of utilizing granular activated carbon depend upon its ability to be regenerated. Regeneration is usually accomplished in a multiple hearth furnace or similar equipment at elevated temperatures in an atmosphere mildly oxidizing to the carbon.

The response of St. Regis carbons to regeneration was determined by comparing spent commercial carbons with spent St. Regis carbons under similar regeneration conditions. Initially, a sample of St. Regis hydropyrolysis char was activated and the surface area was determined. The carbon's capacity for treating mill effluent was obtained utilizing an isotherm determination. The fresh activated sample was then exposed to Pensacola mill effluent to yield a loaded (spent) carbon for a regeneration study.

There was no previous knowledge of the required regeneration conditions for spent St. Regis carbon. Also, the amount of carbon available would permit only two regenerations. For these reasons, granular Atlas Darco was loaded and then regenerated using a number of different conditions and the results of these runs were analyzed to set the regeneration conditions for St. Regis activated carbon.

Atlas Darco was regenerated under a set of conditions varying from nitrogen gas at 500°C for 3 hours to a flue gas mixture at 850°C for 3 hours. All regenerations were performed in a fluid bed furnace. These experiments indicated that Darco could be regenerated under rather mild conditions. This information and a consideration of the high reactivity of St. Regis carbon indicated that a regeneration condition of 600°C in the flue gas mixture for 3 hours would be acceptable. The weight loss for St. Regis carbon under these conditions was higher than anticipated with a regenerated nitrogen surface area of 810 m^2/g. The original activated

carbon had a surface area of 750 m^2/g. As the surface area increased with regeneration, additional activation probably occurred and the conditions chosen were judged too severe. A second regeneration run performed on St. Regis spent activated carbon in nitrogen alone at 850°C and 3 hours of residence time, restored the surface area to 680 m^2/g from a spent surface area of 470 m^2/g. The isotherm tests on regenerated carbons are tabulated in Table 1. The flue gas and nitrogen regenerations of St. Regis carbon were performed at different times and, therefore, the isotherms were not run simultaneously on the same mill effluent. However, fresh Darco was employed each time as a standard so the results can be compared.

The data indicated that Darco can be regenerated to approximately the same level as St. Regis material in nitrogen. However, in an oxidizing atmosphere, Darco required more vigorous regeneration conditions to regain its original capacity. For example, at 600°C in flue gas, Darco was not regenerated to its full capacity. St. Regis activated carbon at these same conditions underwent additional activation, increasing its capacity. The original activated St. Regis carbon had a lower capacity than granular Darco. The further activation performed during the 600°C regeneration step and the resulting increase in loading capacity indicate that the original St. Regis material may not have had a fully developed pore structure for wastewater treatment applications.

The full regeneration of St. Regis carbon at conditions significantly lower in reactivity than required for a present commercial carbon indicates a possible energy advantage for the hydropyrolysis char-based carbon. The lack of sufficient quantities of char and the difference between the fluid bed used and a commercial multiple hearth make judgements as to yield on regeneration impossible.

MULTIPLE HEARTH FURNACE TRIAL PRIOR TO PILOT PLANT START-UP

The laboratory work employed a fluid bed furnace. Pilot plant operation would employ a mulitple hearth furnace not available until later. Arrangements were made to conduct experiments in a multiple hearth furnace in the laboratory facilities of the pilot plant furnace supplier. The experiments were designed to:

(1) Obtain a feel for the relationship between carbon performance in the fluid bed versus a multiple hearth activation furnace. This information would enable rapid prescreening of materials and conditions using the fluid bed.

(2) Gain a knowledge of the testing and sampling procedures required during a furnace run.

(3) Gain operator experience on a multiple hearth furnace to maximize efficiency during pilot plant startup and operations.

TABLE 1. PERFORMANCE OF ST. REGIS CARBON AND ATLAS DARCO ON MILL EFFLUENT

Carbon	Temp. °C	Atmos.	Pensacola No. 2 Mill Effluent: Color Loading At 400 CU	Color Loading At 100 CU	TOC Loading (mg/g) 130 mg/l	90 mg/l	60 mg/l	Pensacola Total Mill Effluent (2): Color Loading At 400 CU	Color Loading At 100 CU	TOC Loading (mg/g) 130 mg/l	90 mg/l	60 mg/l
Granular Darco (Fresh)	-	-	150	60	90	50	23	500	310	70	60	15
Granular Darco (Loaded)	-	-	38	<10	50	16	~5	220	70	40	20	~1
Darco S-51 (Fresh)	-	-	230	68	200	55	10	400	250	80	50	19
Regenerated Granular Darco	600	N_2	170	<10	100	27	5	290	140	~80	32	12
Regenerated Granular Darco	850	N_2	~240	30	50	20	11	400	180	~100	42	15
Regenerated Granular Darco	450	Pseudo Flue Gas	150	<10	34	12	~4	340	180	~80	32	12
Regenerated Granular Darco	600	Pseudo Flue Gas	120	~30	<10	<1	<1	300	140	~100	42	15
St. Regis Carbon (Fresh)	-	-	90	~20	120	15	~2	270	80	65	25	9
St. Regis Carbon (Loaded)	-	-	Neg.	Neg.	25	~2	<1	50	~10	40	3	<1
St. Regis Regenerated	600	Pseudo Flue gas	270	56	300	40	7	400-600(1)	220	90	65	27
			At 200 CU	At 100 CU								
Granular Darco (Fresh)	-	-	90	72	130	55	20					
St. Regis Regenerated	850	N_2	60	36	73	35	15					

(1) Loading extrapolated with no reversion.

(2) Total mill effluent contains the effluent of No. 1 Mill which includes bleach effluent.

It would have been most desirable to operate with hydropyrolysis char. Unfortunately, the required 1000 kg of char was not available prior to pilot plant start-up. As a substitute for hydropyrolysis char, a coke used by some activated carbon producers was obtained.

The furnace operation consisted of five runs including three temperature levels and two residence times. The gas composition in the multiple hearth was determined during each run. The conditions were duplicated in the fluid bed using the same material and gas composition.

A comparison of fluid bed and multiple hearth data is shown in Figure 2, providing a basis for preliminary selection of pilot plant operating conditions. For a given raw material, carbon tetrachloride numbers (weight % pickup of CCl_4 vapor) and bulk density values were found to be quick indicators of the furnace operation.

The operator exposure to the multiple hearth furnace during these runs proved extremely beneficial during later pilot plant work.

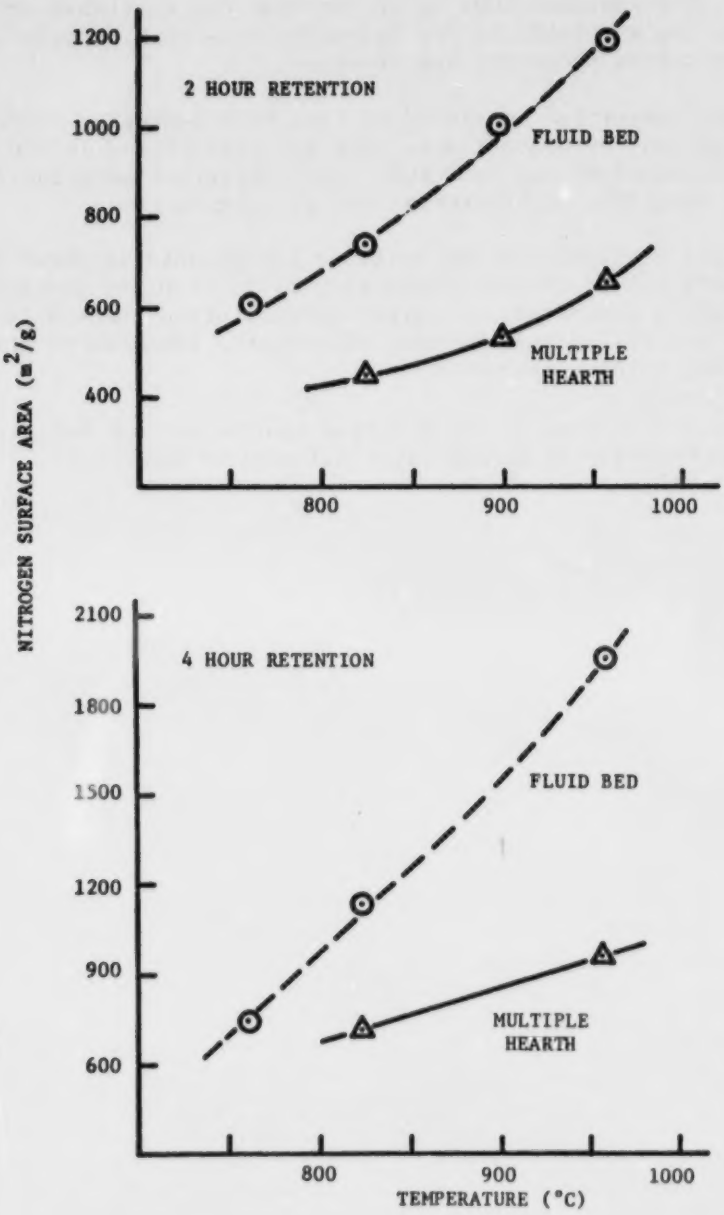


Figure 2. Surface area vs. activation temperature.

SECTION VI

PILOT PLANT DESIGN

DESIGN PROCEDURE

Following a review of the results of laboratory and prepilot operations on October 26, 1971, EPA authorized St. Regis to proceed with Part II of the grant. Pilot plant design efforts began in January, 1972.

A decision was made to use an outside engineering company to design the pilot plant. After preliminary screening, six companies were invited to submit proposals and a contract was awarded in May, 1972. At this time, the engineering contractor was given detailed process flowsheets, material and energy balances, equipment criteria, physical properties of process streams, alternate processing routes, and alternate equipment considerations.

Preliminary cost estimate was considerably higher than anticipated. In order to stay within budget limitation, it was necessary to adopt a number of compromises and simplifications. Major among these was the decision to settle on a single heat exchanger for regenerative heat recovery and a single stage of pressure let-down. The changes made during the design phase will become apparent by comparison of "Description of Process for Design Purposes." which appears later in this section of the report, and "Description of Plant" in Section VII.

BASIS FOR PRELIMINARY ENGINEERING AND SELECTION OF CAPACITY

The absence of commercial or pilot plant experience with hydropyrolysis char, an untried material outside the laboratory, made it impossible to accurately size elements of the char preparation and activation system. This lack of experience was due to the unavailability of sufficient char to perform test work on production equipment. This fact led to two decisions: (1) No attempt should be made to integrate the dry end processes of drying, blending, compaction, and activation into a continuous operation, and (2) No requirement should be imposed which required the dry end of the process to integrate with the wet end in the pilot plant operations. The dry end would then be a batching operation through the several unit operations and operating manpower requirements would be reduced because the wet end and the dry end would not operate at the same time.

Relieved of the requirement of operating as an integrated drying, compaction, and activation train, each component of the dry end was sized at the minimum level for accurate scale-up:

(1) After discussions with several companies which deal in the design of multiple hearth furnaces it was decided that a 0.762 m(30 in) I.D. unit was the minimum that should be installed.

(2) The compactor, a 136 kg (300 lb) per hour minimum machine, would have the greatest capacity of the three components. This size was the smallest available using a commercial configuration. Other units of a laboratory nature with lower capacities were available but were not considered suitable for scale up needs. For lack of better information the compactor was to be designed assuming a carbon black as feed.

(3) The dryer was specified to maintain adequate feed for the expected run time on the dry end.

For wet end (hydropyrolysis char production) design, 2.5 cm (1 in) piping was considered to be the practical minimum in the reactor and heat exchange areas. This fact, combined with the flow velocities required to maintain char in suspension, dictated a nominal feed rate of 0.63 l/sec (10 gpm).

DESCRIPTION OF THE PROCESS FOR DESIGN PURPOSES

The flowsheet given to the engineering contractor as a basis for the preliminary pilot plant design is shown in Figure 3. The process can be broken up into basic unit operations, similar to what was done in connection with Figure 1 in Section IV. These unit processes will be discussed first for the wet end, then for the dry end of the pilot plant.

Wet End

Feed--

The feed to the hydropyrolysis process should be extracted from the mill evaporator system after separation of tall oil soap. At this point in the evaporator system, black liquor has reached approximately 25% solid concentration. Storage at the mill source of black liquor should be sufficient to provide at least two days supply to the pilot plant.

From the storage tank in the mill, the liquor should go directly to holding tanks at the pilot plant. These holding tanks can be used for the gas recycle operation. For the pilot plant design, the gas recycle operation will be simulated by absorbing gases from cylinders into the liquor, using some type of in-line mixing device. The gas will be injected into the liquor while recirculating the contents of the holding tanks.

Pressurization--

This operation, being a continous pressurization process, can be best accomplished through the use of some type of pump. Possible types include a staged-centrifugal, reciprocating piston, or reciprocating plunger pump.

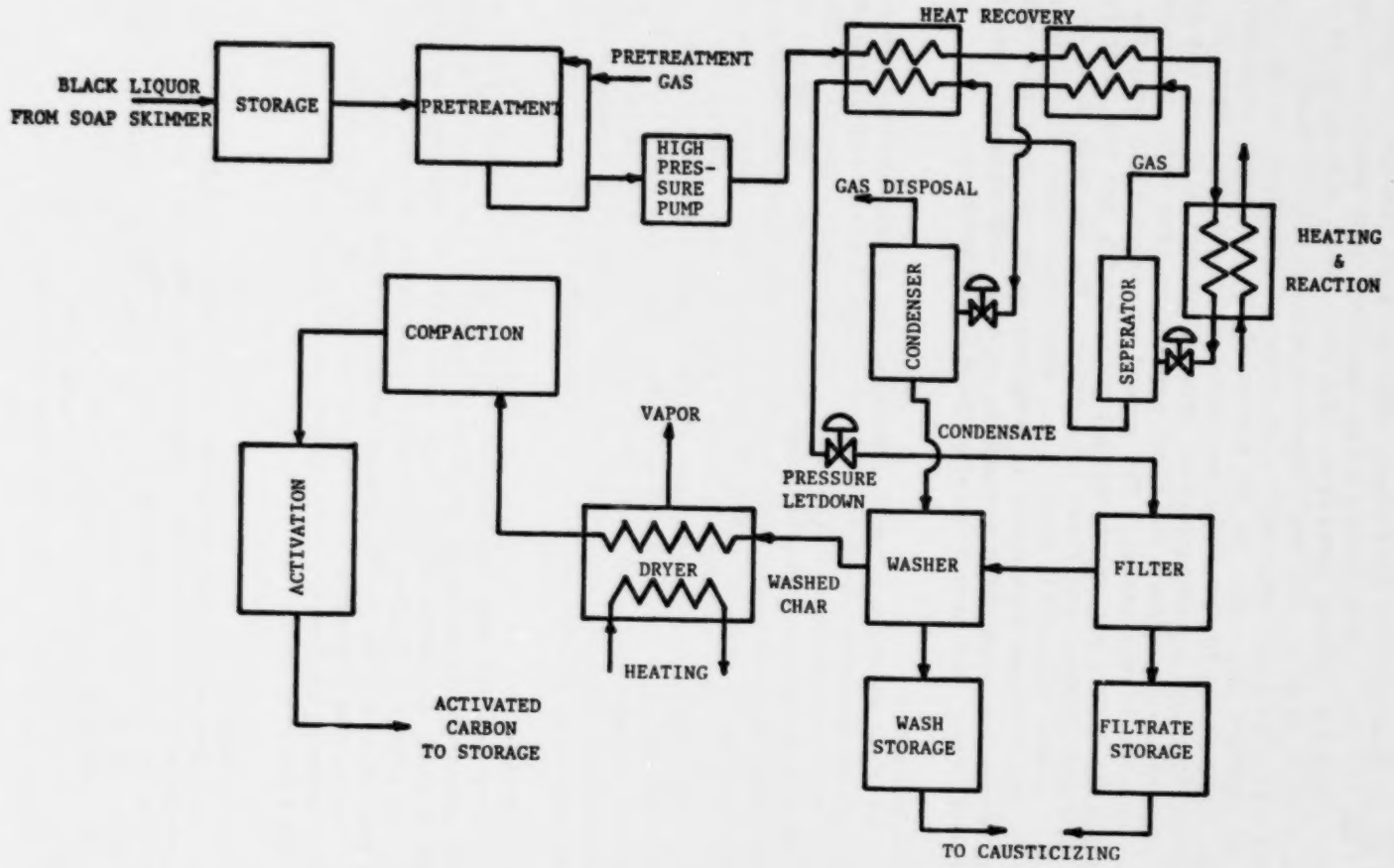


Figure 3. Flow diagram for preliminary pilot plant design.

Heat Recovery--

In order to discuss this operation, since it will involve the recovery of energy from the hot slurry stream after reaction, some mention of the reaction and pressure letdown operations will have to be made prior to discussing them in detail. The heat recovery section should consist of two heat exchangers. The first exchanger (the order of numbering is the same as the order of temperature, i.e., as the number of the exchanger increases, the average temperature in the exchanger increases also) shall heat the treated black liquor by a countercurrent thermal contact with the hot slurry from the first pressure letdown and flash separation (the order of numbering here is the reverse of the above). The second exchanger shall heat the treated liquor by a countercurrent thermal contact with the hot vapor from the first pressure letdown and flash separation. The two heat exchangers can be of any common industrial type, i.e., shell and tube, double pipe, etc. The design of these exchangers is complicated by the fact that streams exchanging energy are under high pressures, at high temperatures, consist of multiphase mixtures, and have a complex chemical composition.

Heating and Reaction--

This operation should provide for heating the liquor leaving the second heat exchanger of the heat recovery section to the desired reaction temperature and provide for the heat of reaction. The operation should provide also for the requirements of the hydropyrolysis reaction. The heater will provide the temperature requirement, but the reaction time requirement will have to be provided by another piece of equipment: the reactor. The reactor can be any of the common industrial types, e.g., tubular, continuous stirred tank, etc. The heater can also be any of the common industrial types, or the reactor and heater could be combined into the same unit. As it was in the case with the exchangers in the heat recovery section, the design of the heater and reactor will be complicated by the high process pressure, high process temperature, multiphase mixture, and complex chemical composition.

Pressure letdown--

The slurry product from the reactor should be cooled below 95°C in order to prevent excessive flashing of water when reducing the process pressure. The slurry product is cooled by the heat exchangers in the heat recovery section. The pressure letdown operation occurs in two steps. The first pressure reduction occurs on the slurry stream immediately as it leaves the reactor. The second pressure reduction occurs on the slurry leaving the first heat recovery exchanger. The slurry at this point should be at a temperature less than 95°C.

Flash Gas Separation--

The flash gas separation operation occurs in two steps. The first step occurs immediately after the first pressure letdown. The gas which is separated is used as the heating medium in the second heat recovery exchanger. As this vapor is cooled, the water which it contains is condensed. The second step occurs after the vapor stream has been cooled, has left the second heat recovery exchanger, and has undergone another pressure reduction. The actual flash gas (non-condensible portion) is separated in

this step. The condensate, or liquid which leaves the second step of flash gas separation, is used for washing the filter cake.

Flash Gas Combustion and Recycle--

The flash gas leaving the second step in the flash gas separation is combusted in a waste gas incinerator. In the pilot plant no attempt will be made to recycle the combusted flash gas. Recycle will be simulated by SO_2 cylinder gas.

Liquid-Solid Separation and Char Washing--

The liquid-solid separation operation is best accomplished by filtration. The filtration can be carried out by using any of the common industrial filtration equipment, e.g., rotary vacuum, belt, extractor, or pressure leaf filters. The liquor which is separated from the slurry (filtrate) is sent to a storage tank and from there to the caustic plant in the kraft mill. The char from filtration goes to washing where any entrained filtrate is washed away. Again, the best way to accomplish this operation would be with industrial filtration equipment. The wash liquor goes to storage and from there to the caustic plant. The washed char will be collected and stored in some type of portable equipment.

Dry End

Drying--

The washed char from the wet end must be dried before the operations of compaction and activation can be performed. Any common industrial dryer can be used for this purpose, e.g., batch vacuum, continuous direct fired or continuous indirect fired dryer.

Compaction--

After drying, the char is compacted to a certain particle size and is then ready for activation. The compactor, for lack of better information, will be designed assuming a carbon black feed.

Activation--

The activation will be carried out on granular rather than powdered char. The type furnace desired is the Herrshoff, or multiple hearth. After activation, the carbon will be stored in some type of portable equipment.

Alternate Processing Routes and Equipment Consideration

Several alternate processing routes, which consisted of modifications made to the flowsheet as shown in Figure 3, were suggested to engineering contractor for consideration. Also, several equipment designs or configurations were suggested for his consideration. Due to the proprietary nature of these matters, they will not be discussed in any detail.

Basis for the Detailed Design and Preparation of the ~~bid~~ Package

As mentioned earlier, the pilot plant cost indicated by the preliminary estimate was much higher than had been anticipated. Therefore, steps were taken to reduce the cost of the pilot plant. This was achieved by modifying

the basic flowsheet as shown in Figure 3 and eliminating the expensive alternate processing routes. The equipment selected for each operation was chosen as the least expensive item that still allowed for operation of the pilot plant as an experimental data gathering unit. Simplified instrumentation, controls, and piping were used in as many places as possible in order to reduce costs.

A major process revision consisted of removing the first pressure letdown and flash gas separation step. The revised process flowsheet is shown in Figure 4. This flowsheet shows the process upon which the detailed design and bid package were based. It should be noted that with the removal of the first pressure letdown and flash gas separation units, some heat exchange capacity was sacrificed in the heat recovery area. Because of this, a heat exchanger to cool the slurry below 95°C was added upstream from the pressure letdown unit.

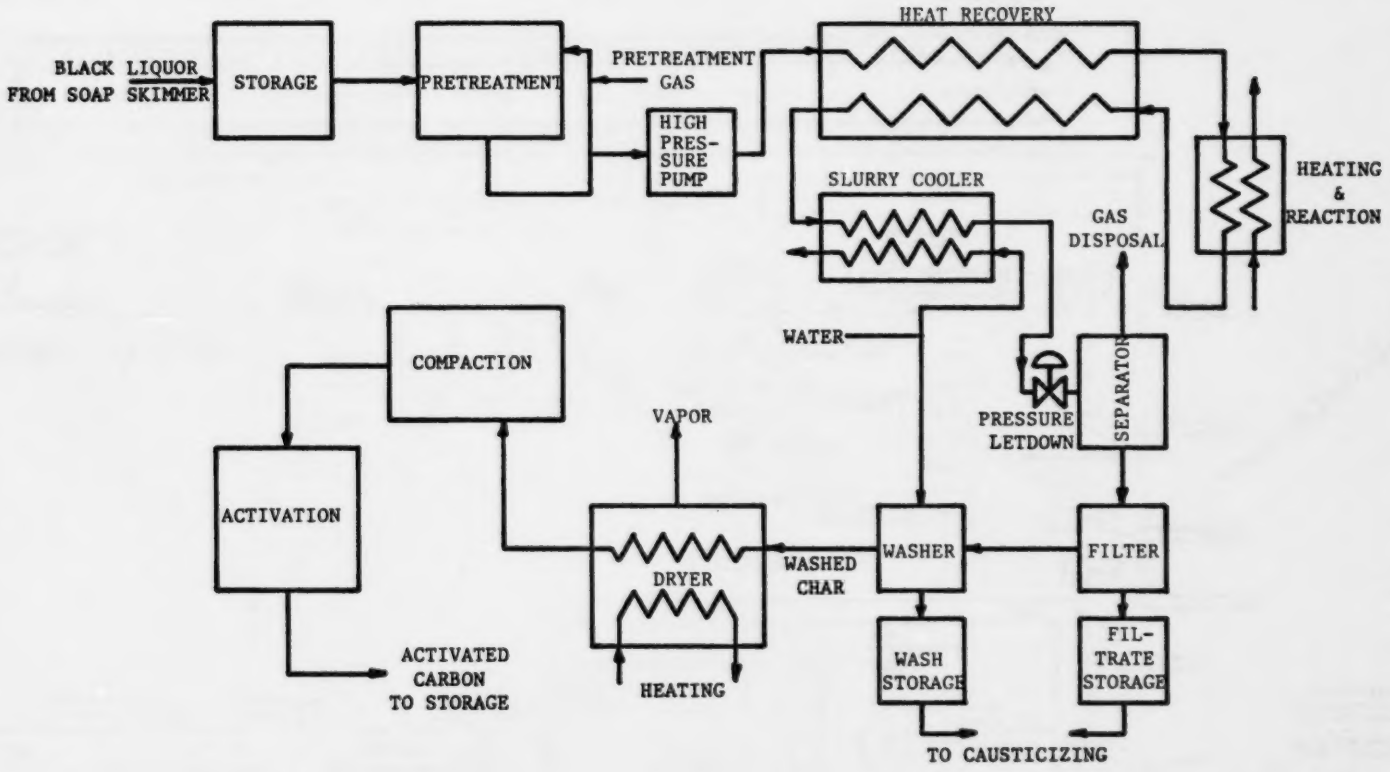


Figure 4. Flow diagram for detailed pilot plant engineering.

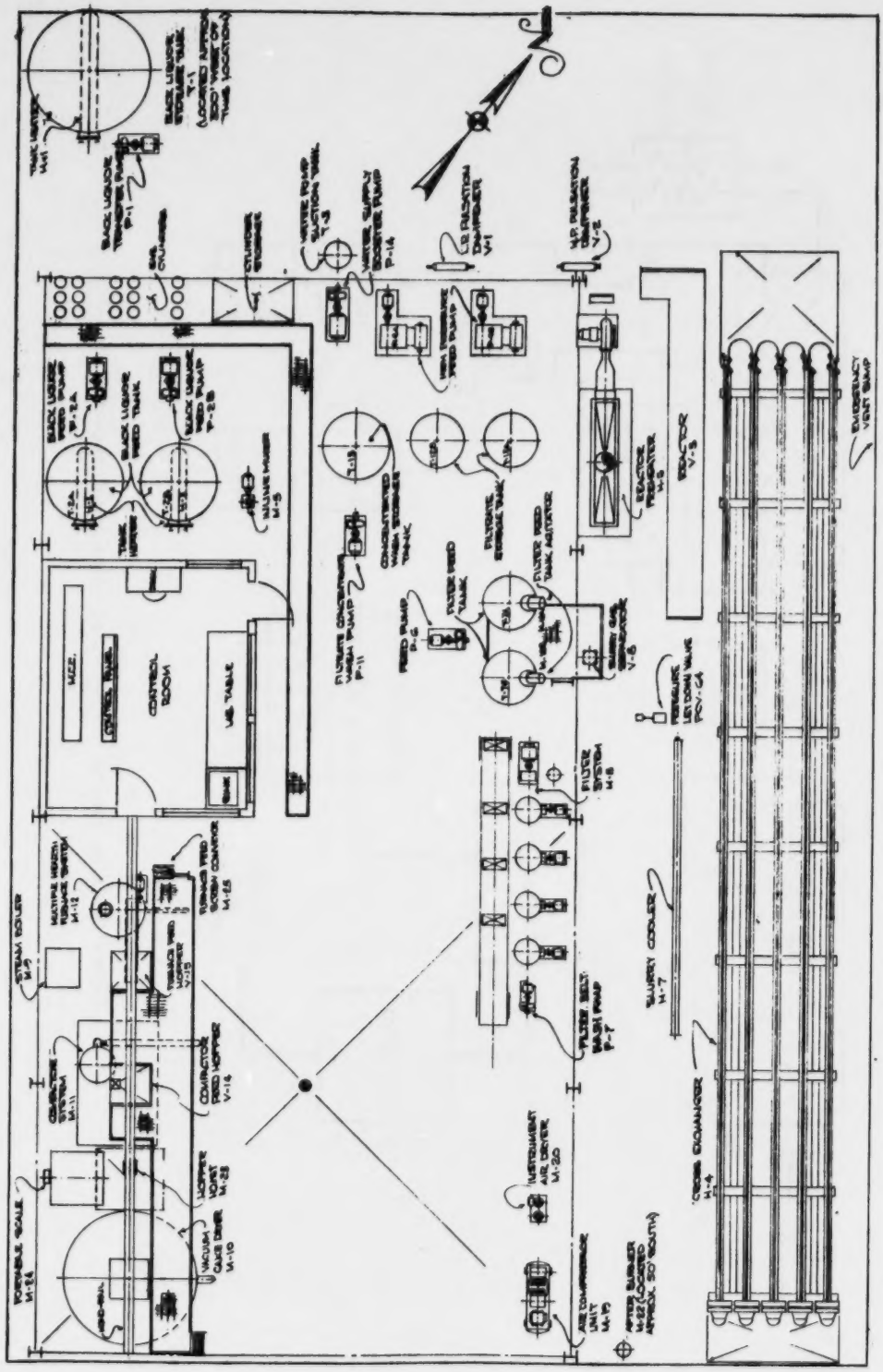


Figure 5. Pilot plant layout drawing.

SECTION VII

PILOT PLANT CONSTRUCTION AND DESCRIPTION OF PLANT

SUMMARY OF THE CONSTRUCTION PHASE

Six construction companies, which previously had expressed an interest in bidding on the job, were provided with the bid package prepared by the design engineers and were invited to bid. Bids were received from five of these on March 1, 1973; the sixth company did not bid. Bids were analyzed and it was recommended that a contract be awarded to the low bidder. A contract was signed in April. Construction began in May, 1973 and was completed in May, 1974.

LAYOUT AND PILOT PLANT EQUIPMENT DETAILS

Figure 4 (Section VI) showed the pilot plant basic flow sheet. Figure 5 is a layout drawing of the plant showing the arrangement of major equipment installed. These two figures should be used for orientation in connection with the plant description below. Also, Figure 6, a general view of the pilot plant from the north, will help the reader to visualize the arrangement in the layout drawing.

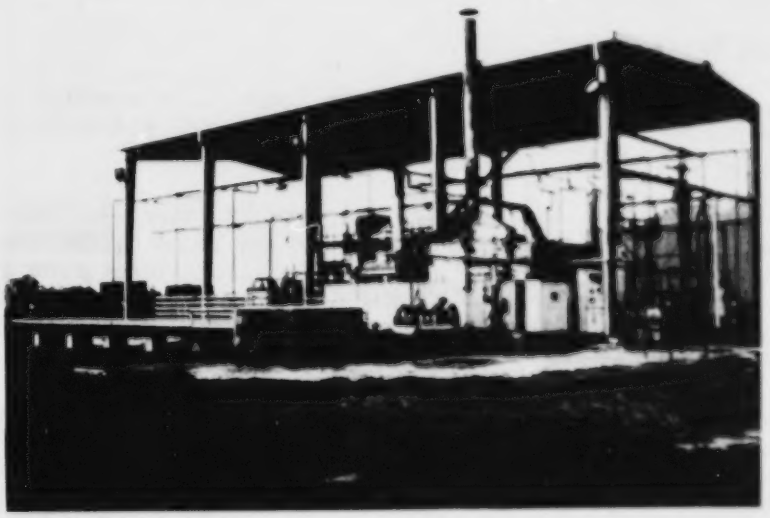


Figure 6. General view of pilot plant.

In the foreground, the cross exchanger, reactor preheater, reactor, and slurry cooler can be seen very easily. Feed pretreatment and the high pressure feed pumps are toward the right rear of the picture. The filter-washer and dry end equipment are hidden to the rear in this view.

Black Liquor Storage

The equipment in this area consists of the black liquor storage tank (T-1), storage tank heater (H-1), and black liquor transfer pump (P-1). (Refer to Figure 5 for equipment designation). This equipment is not located in the pilot plant, but is near the evaporators in the No. 2 pulp mill approximately 100 m west of the pilot plant. This area is connected with the pilot plant by a 10 cm (4 in) carbon steel transfer pipe.

The black liquor storage tank is a 2.74 m (9 ft) diameter by 3.20 m (10.5 ft) high vertical, cylindrical vessel with a 18.9 m^3 (5000 gal) capacity. The tank is fitted with a 0.46 m (1.5 ft) high self supporting conical head. It was designed to operate at atmospheric pressure and to hold black liquor at temperatures in the range 65 to 95°C. The tank is constructed of 0.64 cm (1/4 in.) carbon steel plate and insulated. The tank is connected to the fourth effect evaporator inlet and outlet so 25% or 30% black liquor solids can be drawn off. The purpose of this storage tank is to allow the pilot plant to operate independent of evaporator operation.

The storage tank heater is mounted on the black liquor storage tank for the purpose of keeping the black liquor hot. The heater is a 7.5 kw unit with an immersion element.

The black liquor transfer pump is a ductile iron centrifugal with a 5.59 kw (7.5 hp) motor. It was sized to deliver 4.73 l/sec (75 gpm) when pumping black liquor at 82°C and 31.5 $kkgf/m^2$ (45psig) discharge pressure.

Black Liquor Pretreatment

The equipment contained in the pretreatment area consists of the black liquor feed tanks (T-2A and T-2B), tank heaters (H-2 and H-3), black liquor feed pumps (P-2A and P-2B), and the inline mixer (M-5).

This area of the pilot plant is pictured in Figure 7. The inline mixer can be seen at the extreme lower left. The two large cylindrical vessels are the black liquor feed tanks. One of the black liquor feed pumps can be seen in the lower middle section of the figure. Some of the gas cylinders and the manifolds to which they are attached can be seen in the lower right hand portion of the picture.

The black liquor feed tanks are each 1.68 m (5.5 ft) diameter by 3.66 m (12 ft) high vertical, cylindrical vessels with dished heads. The capacity of each tank is 7.6 m^3 (2000 gal). The design pressure and temperature were 3.5 $kkgf/m^2$ (5 psig) and 65 to 95°C. The material of construction is 0.95 cm (3/8 in) carbon steel plate. Each tank is insulated. The 10 cm (4 in) pipe from the black liquor storage area is connected to each of the tanks. Each tank is connected to the inline mixer.

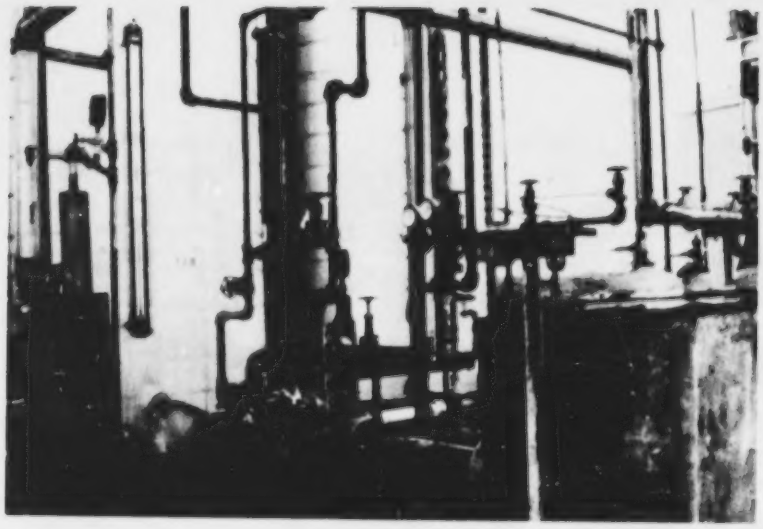


Figure 7. Black liquor pretreatment equipment.

Each of the black liquor feed tanks is equipped with a tank heater. Heater H-2 is a 66 kw immersion type-unit; heater H-3 is a 4.5 kw immersion-type unit.

The black liquor feed pumps are ductile iron centrifugal pumps with 4.73 kw (7.5 hp) motors. The design capacity was 3.15 l/sec (50 gpm) when pumping black liquor at 82°C and 39.2 kkgf/m^2 (56 psig) discharge pressure. The pumps circulate liquor from the tanks T-2A and T-2B through the inline mixer and back to T-2A and T-2B. These pumps also feed treated liquor to the high-pressure pumps P-4A and P-4B.

The inline mixer is a device used to blend components in the process pipe line. The mixer fits directly into the pipe line. It has a mixing chamber with about 7.6 l (2 gal) capacity. The liquid from the process pipe line flows in one end of this chamber and out the other. In the center of this chamber is an agitator paddle. The gas is injected into the bottom of the chamber. The agitator is driven by a 0.75 kw (1 hp) motor. The material of construction is stainless steel.

This operation simulates the recovery of combusted product gas from the process. Normally, only the sulfur dioxide component of the product gas is simulated but the system also provides for nitrogen, oxygen, and carbon dioxide gas feeds.

Pressurization

The equipment contained in the pressurization area consists of the high pressure feed pumps (P-4A and P-4B), low pressure pulsation dampener (V-1), and high pressure pulsation dampener (V-2).

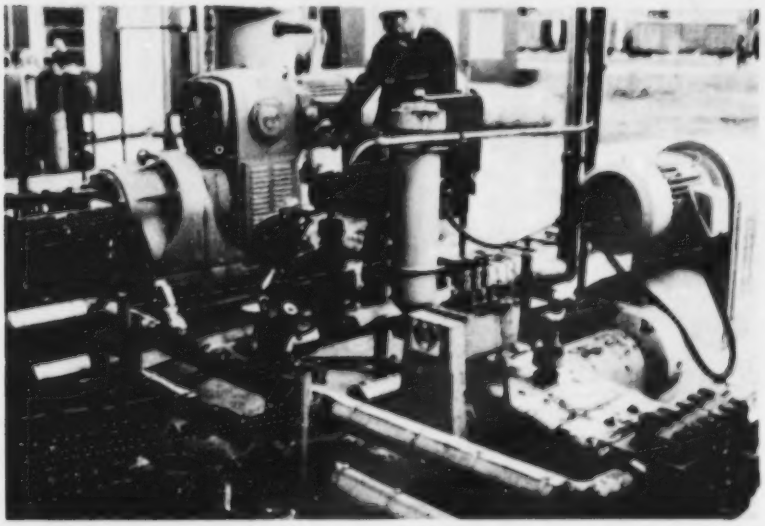


Figure 8. Pressurization equipment.

The actual area in the pilot plant is show in Figure 8. The two pumps are clearly visible. Two pipe manifolds are seen in the lower portion of the picture. The upper manifold is the pump inlet and the lower manifold is the pump discharge. The low pressure pulsation dampener is the cylindrical vessel in the central portion of the picture. The high pressure pulsation dampener is not visible in this picture, but it can be seen in a picture showing the reactor preheater (Figure 11).

Both of the high pressure feed pumps are reciprocating triplex plunger pumps with 22.4 kw (30 hp) motors and variable speed drives. The pump heads, being in contact with the process fluid, are 316 stainless steel. In the pump P-4A, the valves are hardened stainless steel but in P-4B, the valves are normal stainless steel. The pumps discharge into a 316 stainless steel 2.5 cm (1 in) Schedule 80 pipe manifold.

The low pressure pulsation dampener is located on the line that feeds the high pressure feed pump inlets. Its purpose is to reduce the liquid pulsation pressure in the suction line of the high pressure plunger pumps. This pulsation dampener is a cartridge type which uses nitrogen gas for stabilization. It has a volume capacity for 4.9 l (300 in ^{3}) of nitrogen gas.

The high pressure pulsation dampener is located on the line leading from the discharge of the high pressure feed pumps. Its purpose is to reduce the liquid pulsation pressure in the discharge line.

Heat Recovery

The equipment contained in the heat recovery area consists of the cross exchanger (H-4). A picture of the cross exchanger is shown in Figure 9. This picture shows the cross exchanger as viewed from the front of the pilot plant at about waist level. An additional view of this large piece of equipment can be seen in Figure 6.

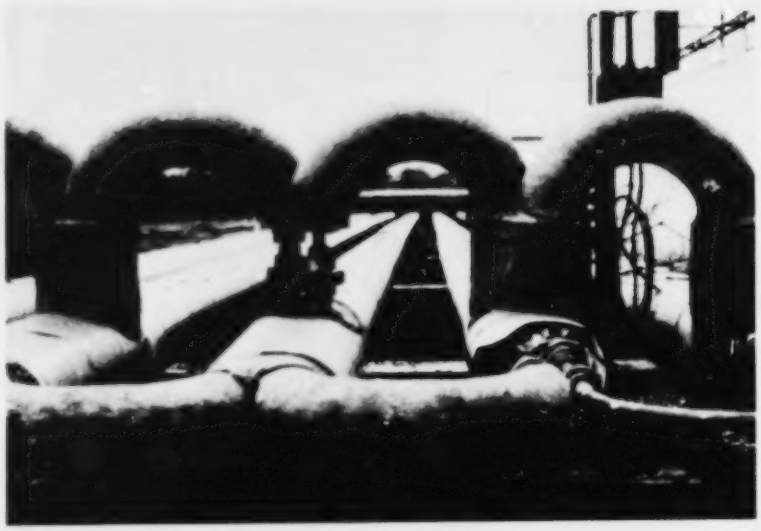


Figure 9. Cross exchanger.

The cross exchanger is a double pipe heat exchanger with 5 hairpins. The inner pipe is 2.5 cm (1 in) Schedule 80; the outer pipe is 5 cm (2 in) Schedule 160. Both are 316 stainless steel. The cross exchanger was designed so that the inner pipe can be removed for cleaning.

The cross exchanger heats the feed stream to a temperature approaching the desired reaction temperature by regenerative heat exchange with the product stream, thus cooling the product stream and achieving heat economy.

Heating and Reaction

The equipment contained in the heating and reaction area consists of the reactor preheater (H-6) and reactor (V-3). Views of the reactor preheater and reactor from the front of the pilot plant are shown in Figures 10 and 11. The cyclindrical vessel in the upper middle portion of Figure 11 is the high pressure pulsation dampener.

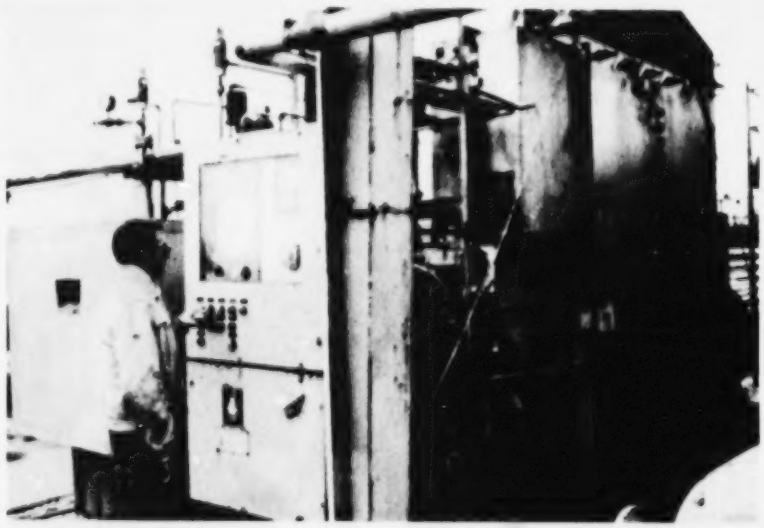


Figure 10. Heating and reaction equipment.

The reactor preheater is a convection type, non-radiant heater which utilizes natural gas as fuel. The process fluid makes thermal contact with the heating medium by flowing thru 316 S.S. 2.5 cm (1 in) Schedule 80 pipe.

The reactor is an adiabatic tubular reactor. The actual tubular portion of the reactor is constructed of 316 S.S. 3.8 cm (1.5 in) Schedule 80 pipe. The reactor is made adiabatic by an insulated rectangular box around the pipe bundle.

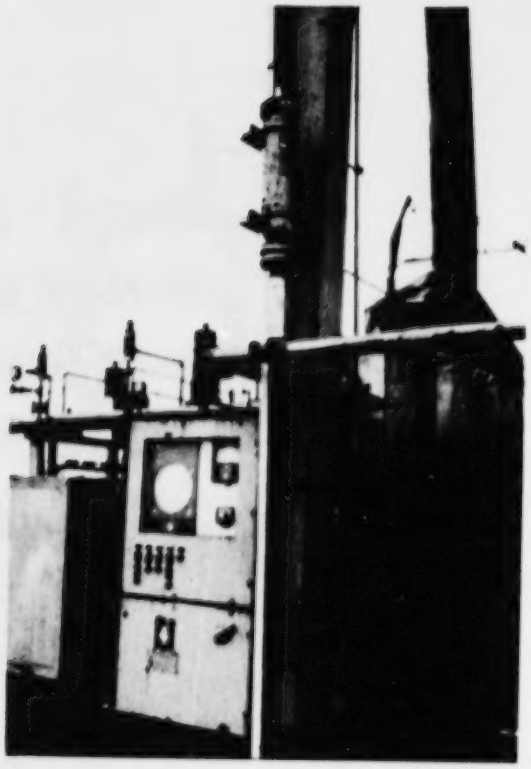


Figure 11. Heating and reaction equipment.

Pressure Let-down

The equipment contained in the pressure letdown area consists of the slurry cooler (H-7) and the pressure let-down valve (PCV-64). A picture of this area is shown in Figure 12. The pressure let-down valve can be seen in the middle left portion of the picture. The slurry cooler is seen in the right hand portion of the picture.

The slurry cooler is a heat exchanger used to cool the slurry from the cross exchanger below 95°C. This is necessary before the pressure let-down operation can be carried out; otherwise the water in the slurry would flash. The slurry cooler is a double-pipe, six-hairpin, heat exchanger with slurry flowing through the inner pipe and water flowing through the annular space between the inner and outer pipes. The inner pipe is 316 S.S. 2.5 cm (1 in) Schedule 80 pipe, while the outer pipe is a carbon steel 5 cm (2 in) Schedule 40 pipe.

The pressure letdown valve is a 1.27 cm (1/2 in) angle-body control valve. The body is constructed of 316 S.S., and the trim is linear with C_v of 1.5. The trim is constructed of stellite.

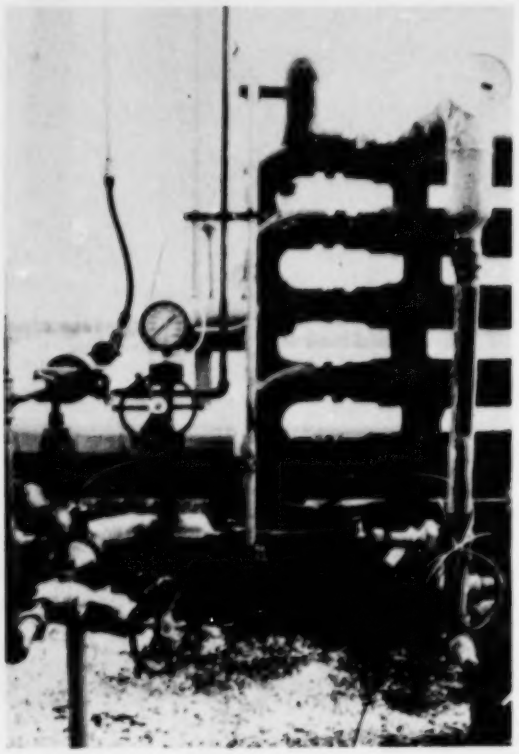


Figure 12. Slurry cooling and pressure let-down equipment.

Flash Gas Separation

The equipment contained in the flash gas separation area consists of the slurry-gas separator (V-8). A picture of the slurry-gas separator is shown in Figure 13. This is a view of the separator as one would see it when standing next to the pressure let-down valve. The separator is the cylindrical vessel in the right hand portion of the figure.

The slurry-gas separator is a cylindrical vessel 0.32 m (12.75 in) in outside diameter and 1.83 m (6 ft) in height. The vessel is constructed of 316 S.S. The design pressure and temperature was 3.5 kkgf/m^2 (5 psig) and 95°C. The vessel is insulated. The separator is connected to the pressure let-down valve. (316 S.S. 2.5 cm 1 in). Schedule 80 pipe was used for interconnecting all the equipment from the high pressure feed pump discharge to

the separator inlet, The slurry which leaves the separator and flows to the filtration area exits from the bottom of the separator by a 3.8 cm (1.5 in) carbon steel pipe. The gas outlet is at the top of the separator. A 316 S.S. 5 cm (2 in) Schedule 10 pipeline connects the separator gas outlet with flash-gas combustion.

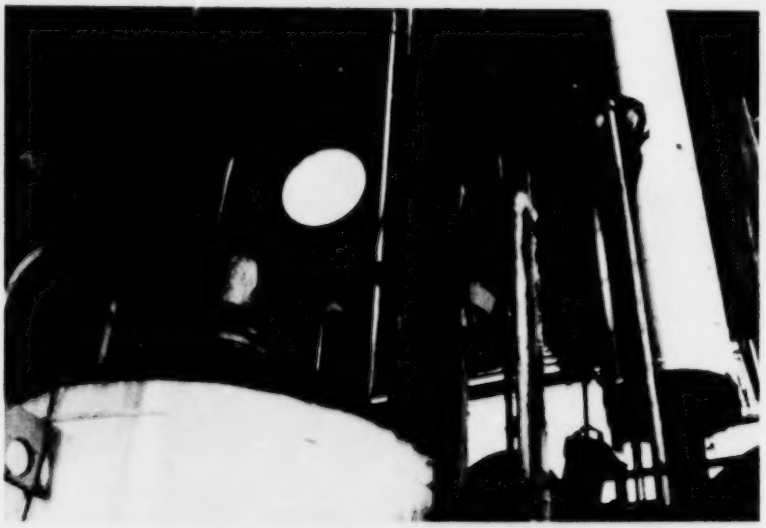


Figure 13. Slurry-gas separation equipment.

Flash Gas Combustion

The equipment contained in the flash-gas combustion area consists of the afterburner (M-22) shown in Figure 14.

The afterburner is a self-supporting, natural-gas-fired, incinerator for gases that are produced in the hydropyrolysis reaction. Its purpose is to oxidize the gas products from the slurry-gas separator and the filter system vacuum pump discharge. The unit is failure safe, operating with a positive ignition pilot system to maintain a continuous flame.

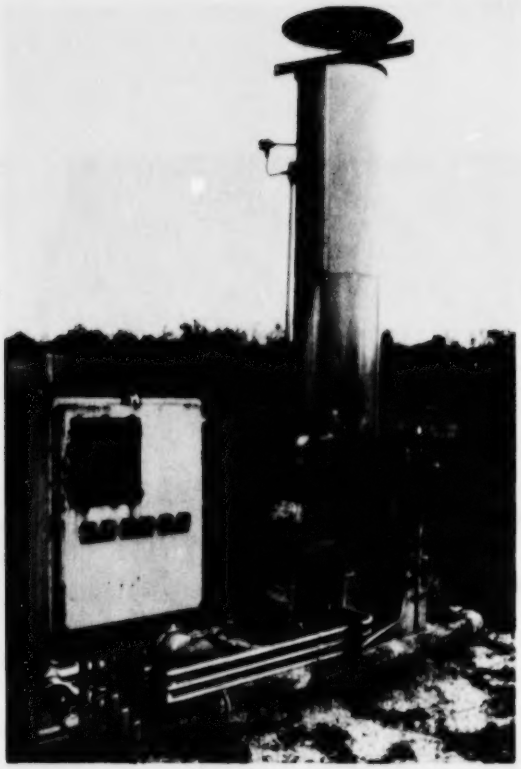


Figure 14. Flash gas combustion equipment.

Liquid-Solid Separation and Char Washing

The equipment contained in the liquid-solid separation and char washing area consists of the filter feed tanks (T-7A and T-7B), filter feed tank agitators (M-18A and M-18B), filter feed pump (P-6), filter system (M-8), filter beltwash pump (P-7), filtrate storage tanks (T-12A and T-12B), concentrated wash storage tank (T-13), and filtrate-concentrated wash pump (P-11). A picture of the filter system as viewed from the south end of the pilot plant is shown in Figure 15. In this figure, the belt drum drive, cloth discharge roll, and vacuum manifold can be seen clearly. In the upper left hand corner of the figure, the slurry-gas separator can be seen. In the middle left hand portion of the figure, the filter feed tank (T-7B) can be seen.

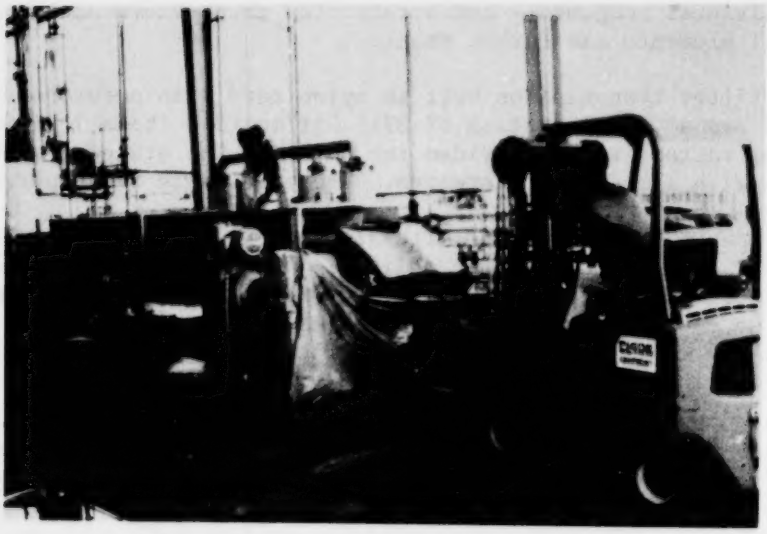


Figure 15. Filtration and washing equipment.

The filter feed tanks T-7A and T-7B are identical. Each tank is a 1.23m (4 ft) diameter by 1.68 m (5.5 ft) high cylindrical vessel with 0.30 m (1 ft) deep conical bottom. The capacity of each is 1.9 m^3 (500 gal). The material of construction is carbon steel and each tank is insulated.

The filter feed pump (P-6) is a ductile iron centrifugal pump with a 0.56 kw (3/4 hp) motor. It is connected to the filter feed tank recycle lines and the filter system feed line by a 2.5 cm (1 in) carbon steel manifold. The filter belt wash pump (P-7) is a cast iron centrifugal self priming pump with a 0.37 kw (1/2 hp) motor.

The filter feed tank agitators M-18A and M-18B are 26.7 cm (10.5 in) propeller type agitators with a single impeller. The shafts are carbon steel and the propellers are stainless steel. The agitators have 0.56 kw (3/4 hp) motors with variable speed drives. They operate from 0 to 350 rpm.

The filter system M-8 is a top feed extractor belt filter which continuously dewaters and washes the hydropyrolysis char. The filter is approximately 6.1 m (20 ft) long with a 0.30 m (1 ft) wide transmission belt. This provides about 1.67 m^2 (18 ft^2) of active area. The unit is skid mounted with all accessories including controls, control panel, motors, safety devices (overload protection, branch circuit fuses, etc.), and control voltage transformer prewired to single end point connections. Piping between individual components and accessories is provided on the skid. All structural elements are carbon steel.

The filter transmission belt is nylon cord with neoprene external cover and has a tensile rating of 37.5 kgf/cm (210 lb/in) of width. Stainless steel fasteners are provided for joints. The drainage grids are polypropylene with steel grid fasteners. The edge seals are neoprene.

The vacuum box is made of mild steel with four compartments and four outlets. The cloth belt filter medium is nylon and has a stainless steel clipper lace. After cake discharge, two spray pipes are provided for washing the cloth. The spray pipe nozzles are V-jet type on 6.35 cm (2.5 in) centers. A fiberglass reinforced polyester wash collecting pan is provided for the full length of the filter.

The extractor top feed assembly is composed of four steel overflow weir boxes: one for the hydropyrolysis slurry feed and three for the wash water feed to the wash stages. The hydropyrolysis slurry feed box has a neoprene wiper material and special side dams and seals for maintaining a slurry pool at the feed end. The filter has a 1.49 kw (2 hp) motor with variable speed drive and a heavy duty enclosed worm gear reducer. The belt speed ranges from a minimum of 0.91 m/min (3 ft/min) to a maximum of 4.57 m/min (15 ft/min).

The following accessories complete the filter assembly:

(1) Four 0.36 m (14 in) diameter by 1.22 m (4 ft) high cylindrical vacuum pump receivers made of carbon steel reinforced for vacuum service.

(2) One cast iron water seal vacuum pump with 10.2 m^3/min (360 cfm) capacity at 559 mm (22 in) of Hg vacuum and 1170 rpm. The vacuum pump motor is 18.64 kw (25 hp) and 1800 rpm.

(3) Four self-priming, centerline discharge, ductile iron, centrifugal filtrate pumps. The pump motors are 1.12 kw (1.5 hp) at 1750 rpm.

The filtrate storage tanks T-12A and T-12B are each 1.23 m (4 ft) diameter by 1.68 m (5.5 ft) high cylindrical vessels with 1.9 m^3 (500 gal) capacity. The tanks are carbon steel, insulated, and have flat tops. Both tanks are connected to the filtrate pump under the first suction box of the filter.

The concentrated wash storage tank T-13 is a 1.52 m (5 ft) diameter by 1.68 m (5.5 ft) high cylindrical vessel with 2.84 m^3 (750 gal) capacity. The tank is carbon steel, insulated, and has a flat top. It is connected to the filtrate pump under the second suction box of the filter.

The filtrate-concentrated wash pump (P-11) is a ductile iron centrifugal pump with a 5.6 kw (7.5 hp) motor. The pump transfers filtrate from tanks T-12A, T-12B, and T-13 to the No. 2 mill green liquor clarifier.

Drying

Equipment in the drying area consists of the vacuum cake dryer (M-10). Figure 16 is a picture of the dryer.

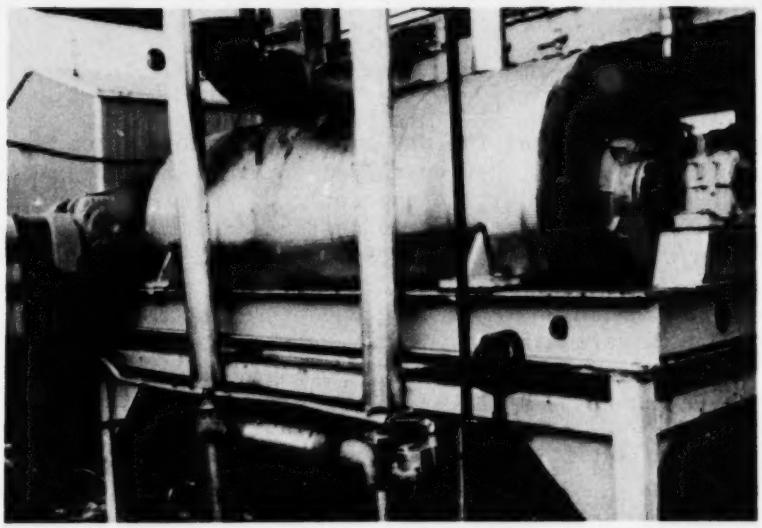


Figure 16. Char drying equipment.

The pilot equipment used to dry hydropyrolysis char is a Stokes Model #59 vacuum dryer. This system is a rotary batch dryer consisting of a stationary cylinder with a rotating central shaft. The capacity, running half full, is 0.283 m^3 (10 ft^3). Welded to the shaft are spiral agitator and scraper blades. The cylinder is jacketed to receive a heating medium, which is steam for the pilot plant. Shell working pressure is 87.9 $kkgf/m^2$ (125 psig) with full vacuum. Maximum temperature rating is 343°C.

The central agitator shaft, but not the blades, is heated by steam. Total heating surface in the shell and shaft is 3.76 m^2 (40.5 ft^2). The agitator, driven at 6 rpm by the 1.12 kw (1.5 hp) drive, continuously mixes *and distributes* the material over the heated surface of the cylinder.

The dryer is charged through the loading port at the top. When the drying is complete, the bottom discharge port is opened and the large outer spirals rapidly sweep the material out of the dryer. Cooling water may be passed through the jacket to reduce char temperature before discharge. Water vapor removed from the char filter cake in the dryer cylinder passes through a vacuum line and enters a shell and tube condenser.

The pilot plant batch dryer is only a tool to produce dry char for subsequent operations. Although the unit can provide some drying rate data, it does not provide full information for selection of production units. When needed, this can be accomplished by testing char samples in dryer vendor facilities.

Blending

The design objective of the dry end of the pilot plant is to produce a granular activated carbon. Hydropyrolysis char is produced as a fine powder and requires compaction to attain the desired particle size. In order for some carbonaceous materials to attain sufficient strength during the compaction to withstand further processing, a binder is sometimes required. Therefore, the plant was equipped with a drum rotator to blend char with a powdered binder. Additional blending equipment was not considered required initially as units were available on a rental basis if necessary.

Early in the pilot operation it was determined that the dryer with its spiral agitators could be efficiently utilized as a blender. Thus the dryer acquired two duties: a batch dryer and batch blender.

Compaction System

The compaction system (M-11) is a unitized assembly of a mixer, feed screw, press rolls, granulator, and screen pack, with associated conveying equipment, manufactured by K. G. Industries (#5274-25CS). Figure 17 is a picture of the assembly and Figure 18 is a schematic drawing of the arrangement.

Feed char is contained in a hopper and flow to the compactor is controlled with a slide valve. The raw feed passes through a mixer where it is blended with recycled fines. The mixer is of the paddle type. The paddles are angled to push the material toward the roll feed screw. Some paddles have reverse angle to back mix the char for better blending. The mixer is driven at a constant speed of 29.2 rpm by a 7.46 kw (10 hp) motor operating through a chain drive and speed reducing gearbox.

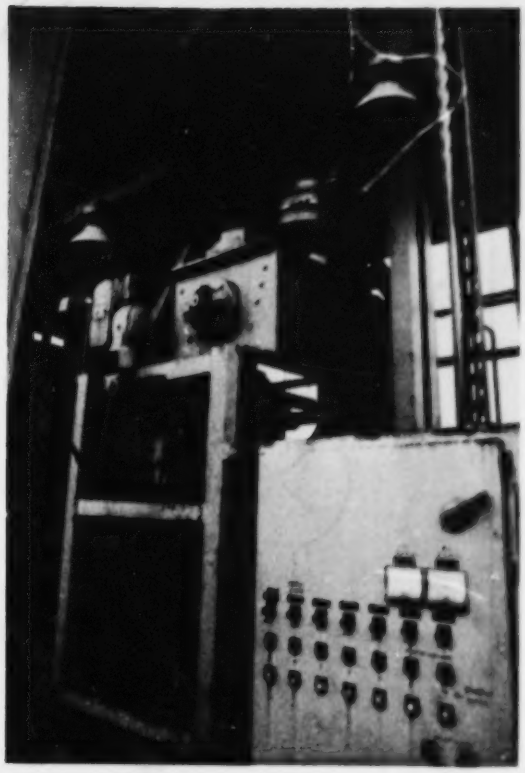


Figure 17. Compaction equipment.

At the end of the mixer, the char drops into the feed screw where the entrained air is pressed out and the char is predensified for optimum press roll operation. The feed screw is highly loaded and is a one piece forging. Speed is variable from 30 to 295 rpm by means of a varispeed drive operating off a 2.24 kw (3 hp) motor.

To accomplish compaction, the predensified material passes between two rolls. These rolls are machined from 440 stainless steel and have corrugated faces. The roll loading force may be varied from 0 to 13,600 kg (30,000 lb). This force is developed with a hydraulic pump and a hydraulic cylinder and lever arm on each roll. An accumulator is included in the hydraulic system to maintain pressure while compensating for variable char

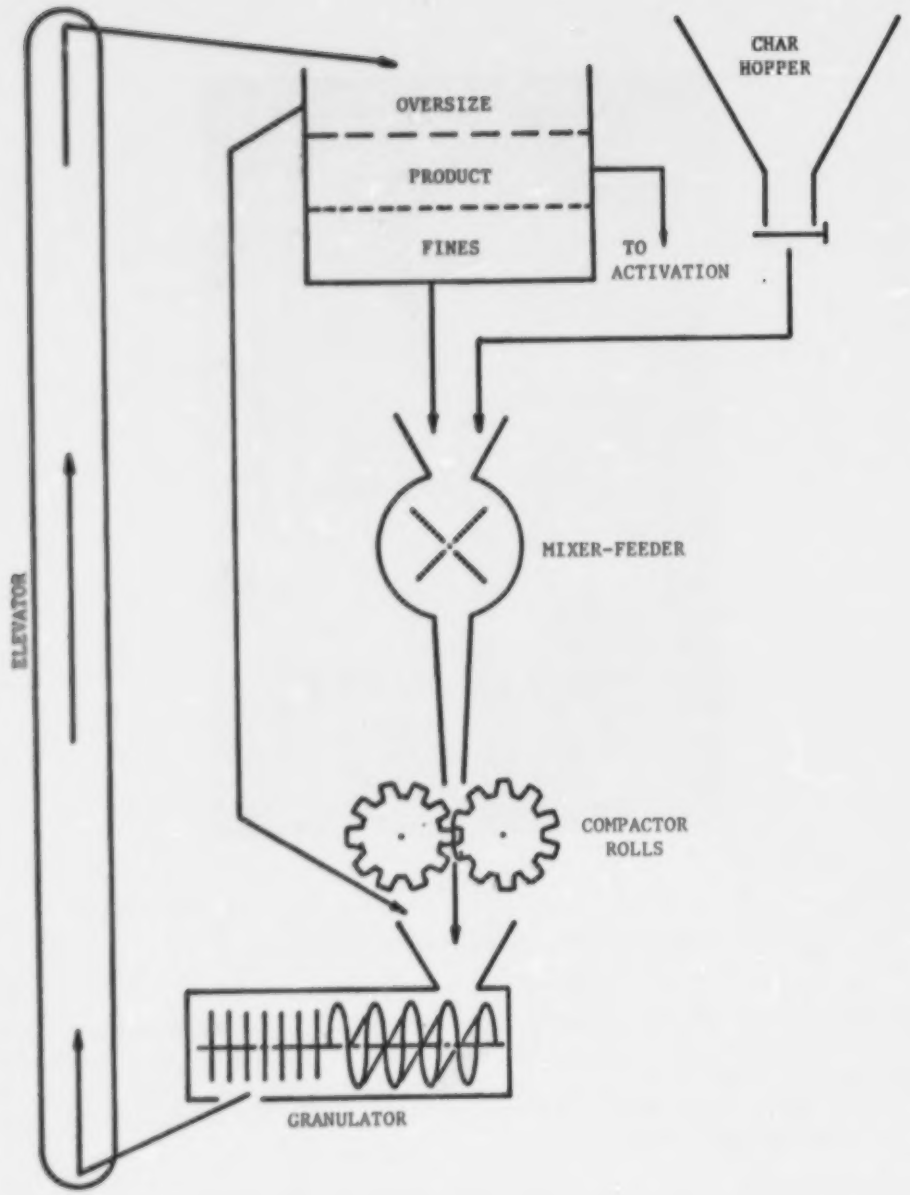


Figure 18. Compactor system schematic.

loading on the rolls. Both rolls are positively driven at 10.5 rpm by a 3.73 kw (5 hp) motor through a gearbox. Roll speed is not variable but can be changed by modifying the gearing in the drive.

The corrugated rolls produce a wavey ribbon of compacted char. This material falls through a chute and is pushed into the granulator knives by means of a feed screw. The knives and screw operate on the same shaft and are driven by a 2.24 kw (3 hp) motor. The char is broken up by the knives until it can pass through the granulator screen spinning around the knives and in opposite direction to the blades. The granulator screen is driven through a variable speed drive of 0.75 kw (1 hp).

Granulated char is transported by means of a bucket elevator powered by a .37 kw (1/2 hp) motor to a Sweco screen. In this screen, the oversize is removed and recycled back to the granulator, and the -7 + 20 product is removed and stored in drums. The fines are recycled back to the mixer to be blended with the raw feed char.

Multiple Hearth Furnace System

The furnace system (M-12) includes a multiple hearth activation (or calcining) furnace, associated firing controls, an afterburner, flue gas scrubber and stack assembled by EIMCO-BSP; Envirotech Systems Inc.

The multiple hearth furnace is pictured in Figures 19 and 20. The furnace consists of six circular hearths of cast refractory construction, stacked vertically. The hearths are 0.762 m (30 in) in diameter. Figure 19 is an outside view of the furnace from the firing side. Gas pressure safety devices are at the bottom of the picture. Five sets of gas burner controls and steam injection controls are shown, each serving one of the hearths. Figure 20 is a view of the hearths with the furnace open and the rabble arm assembly removed. Flue gas exhaust ports are visible.

The furnace is fed from a 304 stainless steel hopper above the furnace. Feed rate is controlled by a calibrated 10 cm (4 in) diameter variable speed screw conveyor. Material passes from the screw directly into the top of the furnace.

Compacted char is dropped onto the periphery of the top hearth, called an "in" hearth, and is rabbled toward the center where it drops to the hearth below, called an "out" hearth. The material is then rabbled toward the outside of this hearth and drops through holes to the hearth below. A vertical rotating shaft through the center of the hearths carries 4 rabble arms per hearth with 5 rabble blades per arm. These blades stir the charge and move it in a spiral path across each hearth. The arms and shaft are 310 stainless steel to resist high temperatures. Commercial units, which contain much larger rabble assemblies, have air cooled arms and in severe duty the arms are insulated. The pilot furnace, owing to its small size, includes neither of these options.

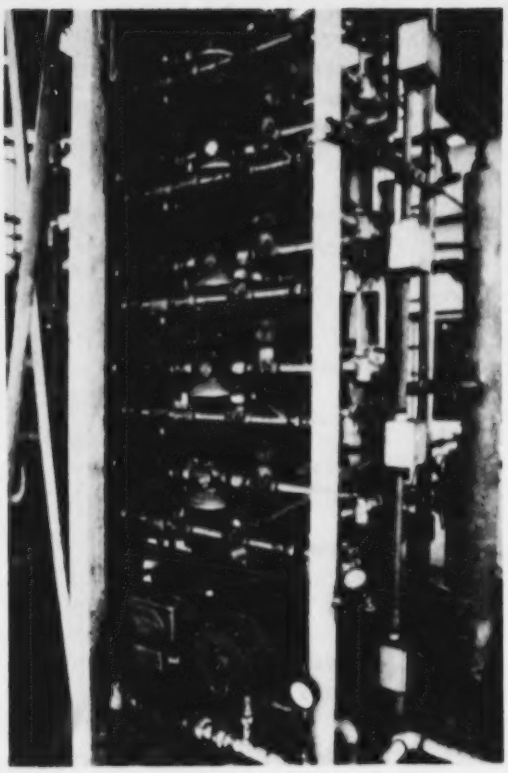


Figure 19. Multiple hearth furnace firing controls.

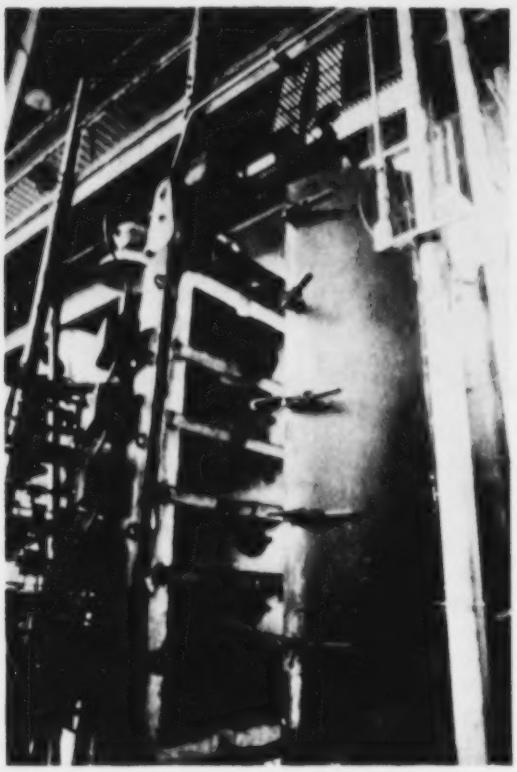


Figure 20. Furnace open for inspection.

The feed passes in and out across the six hearths until it is discharged from the sixth and lowest hearth. The carbon is removed from a chute below the bottom hearth by a 10 cm (4 in) diameter screw conveyor which is water jacketed and contains a water spray. The jacket insures minimum metal temperatures and cools the hot carbon by conduction. Rapid and complete carbon cooling is insured by the spray so that it may be discharged safely. Secondly, the water vaporized by the hot carbon creates a steam blanket and positive pressure in the screw area, lessening the possibility of atmospheric oxygen entering the furnace. This would cause uncontrolled burning of the carbon. All parts in contact with the hot carbon are 304 stainless steel.

Five burner systems are included with the furnace, firing the lower five hearths. This allows maximum flexibility for developing scale-up data. It may not be necessary to fire all of the lower hearths in a commercial installation.

The lower five hearths of the furnace may be fired independently or receive steam injection. Heated gases flow countercurrently to heat the char to reaction temperature and carry on the activation or calcination reactions. Burners are of the nozzle mixing type, wherein the fuel and air are mixed intimately as they enter the burner tunnel. This design prevents flash backs and intraburner explosions. The burners are stable from very high excess air ratios up to 50% excess fuel.

Auxiliary Equipment

Water Supply--

The equipment in this area consists of the water pump suction tank (T-3) and the water supply booster pump (P-14). The water pump suction tank is a 0.61 m (2 ft) diameter by 0.91 m (3 ft) high cylindrical vessel. The water supply booster pump is a ductile iron centrifugal pump with a 14.9 kw (20 hp) motor. It can deliver 11 l/sec (175 gpm).

Steam Boiler--

The steam boiler (M-9) is used primarily to provide steam for the multiple hearth furnace system and dryer; however, small amounts are used to make hot wash water for the filter system and to vaporize the liquid SO_2 from the gas cylinders. The steam boiler is an automatic electric type steam generator capable of operating in the range of 3.5 to 56.3 kkgf/m^2 (5 to 80 psig) with a capacity of 98 kw (10 boiler hp).

Air Compressor--

The air compressor unit (M-19) supplies the air for the pneumatic instruments and for any pneumatically powered equipment in the pilot plant. The compressor has a capacity of 14.16 l/sec (30 scfm) and operates at a receiver outlet pressure of 56.3 kkgf/m^2 (80 psig). The compressor unit has a horizontal air receiver and is a two cylinder, single stage, air cooled unit. A water aftercooler to cool the air to a temperature 5.5°C above the cooling water inlet temperature is provided on the compressor.

Instrument Air Dryer--

The instrument air dryer (M-20) is used to remove moisture from the compressed air prior to its use in the pneumatic instruments. The air dryer is designed to operate at a flowrate of 14.16 l/sec (30 scfm) and at inlet conditions of 70.3 kkgf/m^2 (100 psig) air pressure. The dryer is an electric reactivated dual tower using desiccant for drying. The desiccant is silica gel.

SECTION VIII

OPERATING PROCEDURE

INTRODUCTION

This section describes pilot plant start-up procedure, normal operating procedure, sampling and testing schedule, and the operating schedule. A flow diagram of the pilot plant was shown in Figure 4. This flow diagram and the pilot plant layout shown in Figure 5 should be used for reference in the discussion which follows.

WET END START-UP

The wet end is started up on water. The water pump suction tank (T-3) is filled and the water supply booster pump (P-14) started. This supplies water to the suction of the high-pressure feed pump (P-4). After checking that all upstream and downstream process valves are in their proper position and that the pressure letdown valve (PCV-64) is activated (i.e. fully open), P-4 is started. The variable speed drive selector on P-4 is then set at the position which will deliver the flowrate desired for the run conditions. The control for PCV-64, which is always in the manual mode when the wet end is being started up, is adjusted until the system presure rises to the level desired for the run conditions. When the pressure has become stable, the control for PCV-64 is switched to the automatic mode. At this point, the water is flowing from P-4 through the crossexchanger (H-4) tubeside, to the reactor preheater (H-6), to the reactor (V-3), to the crossexchanger shellside, to the slurry cooler (H-7), to PCV-64, and then to the slurry-gas separator (V-8). During start-up, the water from V-8 is channeled to the trench. After checking that all valves in the line extending from V-8 to the afterburner (M-22) are in their proper position, the after burner is fired off. Next, cooling water is introduced to the shell of the slurry cooler (H-7). At this point, the reactor preheater (H-6) can be started. It has a temperature control unit which controls the process temperature of the fluid exiting H-6. During start-up, the temperature control unit is placed in the manual mode and left there while the system heats up. When the temperature of the process fluid leaving H-6 is within about 15°C of the desired run temperature, the temperature controller is switched to the automatic mode. When the temperature reaches the desired level and becomes steady, the reaction system (this includes the crossexchanger, reactor preheater, and reactor) is ready to process black liquor.

The filter system (M-8) is started up on water. This is accomplished by starting the vacuum pump and the drum roll which drives the transmission belt, then feeding water thru the feed pump (P-6) to the weir box over the No. 1 suction box. Water flowing into the No. 1 vacuum receiver is discarded. Next, water is fed to the filter cloth wash spray nozzles and the filter belt-wash pump (P-7) is turned on. As the water sprays on the filter cloth, it drops to the collection pan located under the filter. The pump (P-7) draws all the water out of this pan and sends it to the feed box over the No. 4 suction box. The water flowing into this feed box is the wash for the char. The wash rate for the run is controlled by the flowrate of water sent to the cloth spray nozzles and is set for the desired run conditions.

The filtrate pumps on all four vacuum receivers are now started. Since the char washing operation is a three stage countercurrent process, the water flowing into the No. 4 vacuum receiver is pumped to the feed box over the No. 3 suction box. The water flowing into the No. 3 vacuum receiver is pumped to the feed box over the No. 2 suction box. The water flowing into the No. 2 vacuum receiver is discarded.

OPERATION ON BLACK LIQUOR

The black liquor storage tank (T-1) always contains enough black liquor to supply the pilot plant for about two days. The storage tank heater (H-1) maintains the temperature in T-1. The amount of black liquor in T-1 is held constant by a level sensing device which is connected to a flow control valve. Whenever it is desired to operate the wet end, the black liquor transfer pump (P-1) is started and the amount of black liquor needed for the run conditions is pumped into the black liquor feed tanks (T-2A and T-2B). The tank heaters (H-2 and H-3) are used to keep the black liquor hot while it is in these tanks.

Pretreatment is a batch operation. There is adequate time during wet section start-up to pretreat the contents of the feed tanks and, during sustained operation, time to pretreat one tank while the other is feeding the system. Black liquor is circulated through the inline mixer (M-5) using either or both black liquor feed pumps (P2A and P2B). Valves to the high pressure feed pump (P-4) suction are closed during pretreatment. Sulfur dioxide gas is added to the black liquor as it circulates through the inline mixer (M-5). After pretreatment, black liquor circulation is continued until the reaction system is ready to receive the liquor.

When the reaction system is ready, treated black liquor is switched to P-4. The water feed to the P-4 suction is shut off and the valves on the recycle line to T-2A and T-2B are closed. At this point, the black liquor is feeding P-4 and being pumped through the reaction system. The water exiting the slurry-gas separator is discarded until the slurry appears. When the slurry appears, the flow is switched to one of the filter feed tanks (T-7A or T-7B). The flash gas will be flowing to the afterburner at this time.

When sufficient slurry has accumulated in T-7A or T-7B, water to the filter feed pump (P-6) is turned off and slurry is fed to P-6 which delivers

slurry to the weir box over the No. 1 suction box on the filter system (M-8). The slurry is separated at the No. 1 suction box into filtrate and unwashed char streams. Filtrate from No. 1 vacuum receiver is switched to the filtrate storage tanks (T-12A and T-12B). At this point the vapor discharge from the vacuum pump is checked to make sure that it is flowing to the afterburner.

When the washed char appears at the discharge roll and begins to fall from the cloth freely, a 208 l (55 gal) drum is placed there to collect the cake. The filter will now run by itself, except for adjustments that have to be made periodically to keep the discharge cake thickness uniform and keep the wash over the No. 2, 3, and 4 suction boxes from flooding.

SAMPLING AND ANALYTICAL PROCEDURES

Samples are taken once during every run when the wet end is running steadily. The following is a list of the process streams which are sampled during a run:

black liquor before pretreatment;
black liquor after pretreatment ;
vapor from V-8;
slurry from V-8;
filtrate (liquor from No. 1 suction box);
unwashed char (char over No. 1 suction box);
concentrated wash (liquor from No. 2 suction box);
washed char (char over No. 4 suction box); and
belt wash (liquid feed over No. 4 suction box).

The samples taken during each run are analyzed in the laboratory using the procedures and analytical equipment described in Appendix A. The results of these analyses, coupled with the flowrate data taken during the runs, allow the construction of material balances. The analytical data also provide characterization of the product streams.

DRY END OPERATING PROCEDURE

The dry end operations of drying, blending, compacting, calcining, and activating were all conducted independently with product storage between operations. (Attempts to calcine on the upper hearths and then activate in the same pass through the furnace encountered control problems. Thereafter, the furnace was set up for either calcination or activation and these operations were conducted separately.) Operating procedures should be apparent from the equipment functional descriptions in Section VII and should require no amplification in this Section.

OPERATING SCHEDULE

The pilot plant operating schedule, as shown in Figure 21, spans a period of 16 months. The pilot plant activities, as covered in this report, began in June 1974 and were completed in September 1975. The schedule can

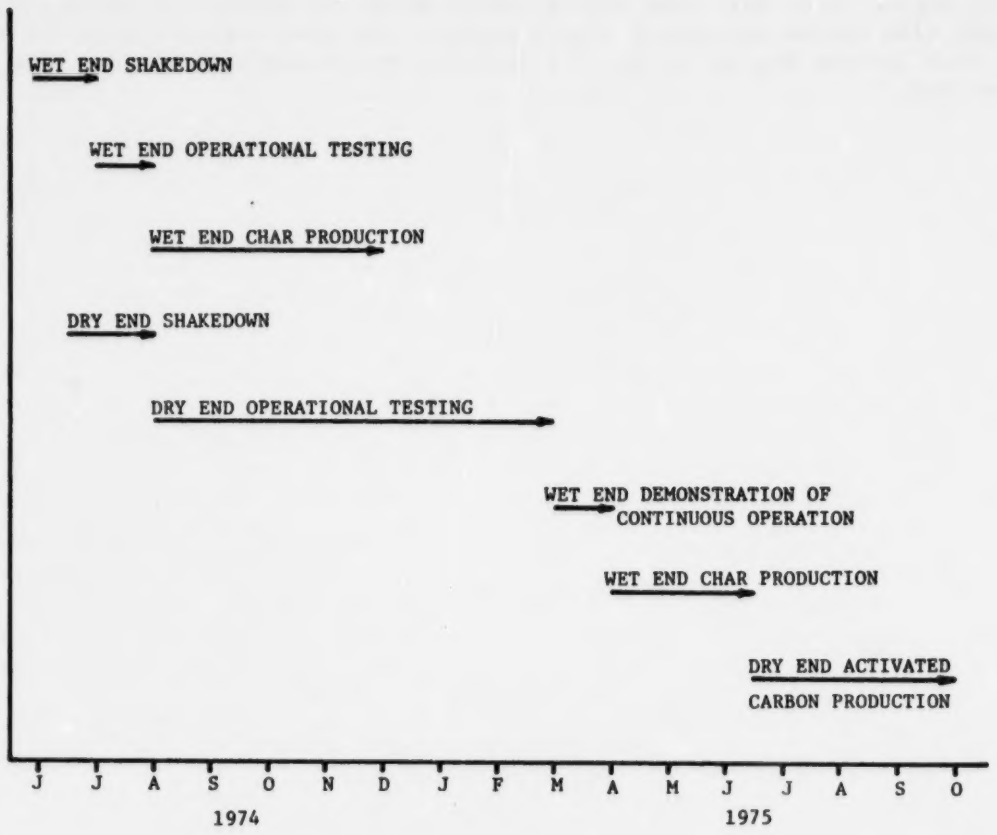

WET END SHAKEDOWN
WET END OPERATIONAL TESTING
WET END CHAR PRODUCTION
DRY END SHAKEDOWN
DRY END OPERATIONAL TESTING
WET END DEMONSTRATION OF CONTINUOUS OPERATION
WET END CHAR PRODUCTION
DRY END ACTIVATED CARBON PRODUCTION
J J A S O N D J F M A M J J A S O
1974
1975

Figure 21. Operating schedule.

be broken down into three periods for the wet end and three similar periods for the dry end.

The shakedown period was the time during which the equipment was debugged and equipment operating procedures were established. The shakedown period for both ends covered a period of 2 months.

The operational testing period was the time when various process conditions were tested to see which conditions would yield an acceptable product. For the wet end, this time period lasted about one month; for the dry end, this time period was spread over 7 months. The time required here was much longer because dry end operations depended on availability of char from the wet end.

SECTION IX

PILOT PLANT OPERATING RESULTS

WET END OPERATIONAL TESTING PERIOD

The operational testing period lasted about one month and was devoted to adjusting process conditions to find the range which would yield a char product suitable for activation. A total of fifteen pilot plant runs was made during this period.

Initial pilot plant conditions were selected based on previous batch and prepilot experience. These conditions were pretreatment to pH 11.5, pressure 1758 kkgf/m^2 (2500 psig), and temperature 345°C (655°F). As expected, pilot plant performance did not precisely duplicate batch and prepilot system performance under the apparently same conditions. It was necessary to adapt and adjust the initial conditions to avoid operating problems and to produce an acceptable char.

There are three primary process variables available for adjustment. These are the amount of SO_2 used for black liquor pretreatment (represented by pH of the pretreated liquor), the operating pressure, and the reaction temperature. The fifteen operational testing runs are summarized in Table 2. The pressure drop (ΔP) across the system is listed as an indication of fouling or plugging. It is the Δ P between the tubeside inlet to the cross exchanger and the outlet from the reactor measured during the heat-up time on water prior to switching to black liquor. The Δ P shown for Run 1 represents a clean system.

The visual appearance of the char product, its filtering ability, and the ability to wash the filter cake are listed to describe the acceptability of the char. "Normal" appearance indicates a fine material, forming a dry-looking cake, which does not flow on standing (not thixotropic). Run 1 produced a char which could not be filtered. The ΔP increased rapidly while running on black liquor and resulted in rupture of several pressure relief discs, terminating the run. It was felt that the rapid increase in Δ P was caused by a salting-out effect brought on by a vapor phase increasing proportionately to the liquid phase in the system. The supposed vapor phase would be incapable of maintaining the solids in suspension and would leave solids deposits on the walls. This explanation later proved to be incorrect but was the basis for selecting pressure and temperature conditions for Run 2.

TABLE 2. OPERATIONAL TESTING PERIOD

Run	Pretreatment pH	Pressure $kkgf/m^2$	Temperature °C	Black liquor solids %	System[a] ΔP $kkgf/m^2$	Char appearance	Filtering ability	Cake washing ability	Running ability
1	11.5	1758	345	N.A	52.7	Tarry	Not filtered	Not washed	Terminated by R.D. failure.
2	11.0	1934	335	25.0	70.3	Grainy	Moderate	Bad	Smooth. ΔP held constant at 70.3 $kkgf/m^2$ on black liquor.
3	11.0	1934	335	32.5	70.3	Grainy	Moderate	Bad	Terminated by R.D. failure.
4	9.5	1934	335	27.5	77.3	Slightly thixotropic	Good	Good	Smooth. ΔP held constant at 87.9 $kkgf/m^2$ on black liquor.
5	10.0	1934	335	30.0	87.9	Normal	Good	Good	Smooth. ΔP held constant at 105.5 $kkgf/m^2$ on black liquor.
6	10.5	1934	335	27.5	87.9	Normal	Good	Good	Smooth. ΔP held constant at 94.9 $kkgf/m^2$ on black liquor.
7	10.5	1934	340	20.0	87.9	Normal	Good	Good	Smooth. ΔP held constant at 87.9 $kkgf/m^2$ on black liquor.
8	10.0	1934	340	30.0	87.9	Normal	Good	Good	Smooth. ΔP held constant at 87.9 $kkgf/m^2$ on black liquor.
9	10.0	1934	340	27.5	87.9	Normal	Good	Good	Smooth. ΔP held constant at 116.0 $kkgf/m^2$ on black liquor.
10	10.0	1934	350	25.0	94.9	No char collected	Not filtered	Not washed	Terminated by R.D. failure.
11	9.5	1934	340	27.5	98.4	Thixotropic	Good	Good	Smooth. ΔP held constant at 105.5 $kkgf/m^2$ on black liquor.
12	9.5	1934	340	30.0	98.4	Thixotropic	Good	Good	Smooth. ΔP held constant at 105.5 $kkgf/m^2$ on black liquor.
13	10.0	1934	340	25.0	87.9	Thixotropic	Good	Good	Smooth. ΔP held constant at 87.9 $kkgf/m^2$ on black liquor.
14	10.0	1934	335	25.0	87.9	Normal	Good	Good	Smooth. ΔP held constant at 105.5 $kkgf/m^2$ on black liquor.
15	10.0	1934	340	30.0	87.9	Normal	Good	Good	R.D. failure (and run termination) was avoided, but ΔP increased from 87.9 at start to 351.6 $kkgf/m^2$ at end of the run.

a) This is the pressure drop through the system on water before the run on black liquor was started.

For Run 2. operating pressure was increased to 1934 kkgf/m^2 (2750 psig) and reaction temperature was decreased to 335°C (635°F). Based on batch and prepilot experience, SO_2 pretreatment was increased to give a pH of 11.0 to improve the properties of the char.

The P on water at the beginning of Run 2 was somewhat higher than the P on the clean system, indicating some build-up of deposits during Run 1. Run 2 proceeded very smoothly on black liquor and the Δ P held steady. The slurry filtered easily and produced a grainy char which looked like black sand. However, the char could not be washed on the three-stage countercurrent extractor belt. All attempts to wash the char resulted in a flooded cloth. In a separate experiment, it was shown that the resistance of this filter cake to the passage of water was very high.

Run 3 was designed to be a duplicate of Run 2. Again, the slurry filtered easily, and a grainy char was produced which could not be washed. The filter cake had a high resistance to the passage of water. Contrary to the experience during Run 2, the Δ P rose rapidly during Run 3 and the run was terminated by pressure relief disc failure. The black liquor received from the mill evaporators for Run 3 had a solids concentration of 32.5% compared to 25.0% solids received for Run 2. It appeared that high black liquor solids concentration contributed to the plugging problem.

In Run 4, feed liquor SO_2 pretreatment was increased further to give a pH of 9.5 System pressure and reaction temperature were unchanged. The Δ P on water before this run reflected deposits which occurred during the previous run. Early in Run 4, there was a further increase in Δ P, perhaps a residual effect of Run 3, then the Δ P held steady, and the run was completed without incident. The slurry filtered easily, the char had "normal" fine-textured appearance and washed very easily on the countercurrent extractor. The filter cake was slightly thixotropic, which presented some difficulty in subsequent solids handling and drying of the char.

In Run 5, the SO_2 pretreatment level was decreased to a pH of 10.0 in search of a level where the filtration and washing would be satisfactory without introducing thixotropic behavior of the filter cake. This objective was realized in Run 5. The run showed no evidence of adding to the deposit problem.

The pretreatment was decreased again in Run 6 to explore the gap between pH's of 11.0 and 10.0. Results were comparable to Run 5.

Runs 5 and 6 defined an area of satisfactory operation and product quality between pH's 10.0 and 10.5. So far, all acceptable runs had been made at one reaction temperature (335°C). In Runs 7, 8, and 9, the temperature was increased 5°C to 340°C and this temperature condition was used in combination with pretreatment in the range of pH's from 10.0 to 10.5. The system operated smoothly and product properties were satisfactory. The Δ P held steady through Runs 7 and 8, making a total of four consecutive runs with no evidence of plugging or deposits. During Run 9, supposedly identical to Run 8, the ΔP rose initially from 87.9 kkgf/m^2 to 116.0 kkgf/m^2, then held constant. The cause of this phenomenon was not understood until later.

It will be remembered that a temperature of 345°C, used in Run 1, resulted in a plugged system. However, the pretreatment and system pressure conditions also were different from those employed in later successful runs. Therefore, it could not be concluded definitely that the 345°C temperature contributed to plugging. Run 10 was designed to use known acceptable pretreatment and pressure conditions at higher temperatures. The reaction temperature was set at 350°C. This is 10 to 15°C higher than the previously demonstrated satisfactory range. Run 10 was terminated almost immediately by excessive pressure which caused relief discs to rupture. Not enough slurry was produced to operate the filter.

In Run 4, (pH 9.5, pressure 1934 kkgf/m^2, temperature 335°C), the system operated well and the only problem with the product char was a slightly thixotropic behavior. The thixotropy was overcome by increasing SO_2 pretreatment. Runs 11 and 12 were made to determine whether a temperature change could have overcome the problem. Pretreatment to pH 9.5 was used with a temperature of 340°C. Both runs under these conditions produced char with greater thixotropy, further demonstrating the unsatisfactory results of pretreatment to pH 9.5. Run 13 used the conditions (pH 10.0, 1934 kkgf/m^2, 340°C) which proved satisfactory in earlier runs but the reactor was by-passed to shorten the reaction time. This run utilized only the cross exchanger and the reactor preheater. There were no operating problems but the char was thixotropic.

At this point, conditions for satisfactory operation and product quality could be defined as pretreatment conditions between pH 10.0 and 10.5, pressure 1934 kkgf/m^2, and temperature between 335°C and 340°C. Run 9, however, which employed conditions within this range, resulted in a Δ P while running on black liquor and left some deposits in the systems. This suggested that the lower temperature might be superior. Runs 14 and 15 were made to test this assumption. Run 14 at 335°C proceeded smoothly. Run 15 at 340°C did not proceed smoothly. Relief disc failure was avoided but the system Δ P increased from 87.9 kkgf/m^2 to 351.6 kkgf/m^2 when the run was stopped. It appeared that the lower temperature was better.

At this point, it was not understood why Runs 8, 9, and 15, all conducted at apparently the same conditions, gave different results. Run 8 proceeded smoothly, Run 9 showed a small increase in Δ P, and Run 15 threatened relief disc failure. Later, it became apparent that the differences reflected the extent of control over the temperature.

PRODUCTION OF CHAR FOR DRY END OPERATIONAL TESTING

At the completion of the wet end operational testing period, conditions had been identified which would yield a char which could be handled and processed in the dry end. A program was initiated to produce the char needed for the dry end operational testing period. Twenty char production runs were made and results are summarized in Table 3. Most of these runs

TABLE 3. PRODUCTION OF CHAR FOR DRY END TESTING

Run	Pretreatment pH	Pressure kkgf/m^2	Temperature °C	Black liquor solids %	System[a] Δ P kkgf/m^2	Char appearance	Filtering ability	Cake washing ability	Running ability
16	10.0	1776	335	30.0	112.5	Normal	Good	Good	Smooth. Δ P held constant at 140.6 kkgf/m^2 on black liquor.
17	10.0	1776	330	30.0	123.0	Normal	Good	Good	Smooth. Δ P held constant at 140.6 kkgf/m^2 on black liquor.
18	10.0	1776	340	35.0	123.0	Normal	Good	Good	R.D. failure in the initial part of the run; but PSV reseated and the run was continued. Run was not terminated, but Δ P rose from 123.0 to 527.3 kkgf/m^2 on black liquor when the run was stopped.
19	10.0	1934	335	25.0	140.6	Grainy	Slurry not filtered	Slurry not filtered	Run was not terminated by R.D. failure, but Δ P rose from 140.6 to 386.7 kkgf/m^2 when run was stopped.
20	10.0	1934	335	25.0	158.2	Run terminated before any slurry could be collected			The run was terminated by R.D. failure. Run time was very short.
21	10.0	1934	340	25.0	105.5	Normal	Good	Good	The run proceeded smoothly with Δ P rising initially to 140.6 kkgf/m^2 on black liquor and holding steady.
22	10.0	1934	340	27.5	130.1	Normal	Good	Good	R.D. failure in the initial part of the run; but PSV reseated and run was continued. This time the run proceeded smoothly with Δ P holding constant at 193.4 kkgf/m^2.
23	10.0	1776	340	25.0	175.8	Normal	Good	Good	Run was not terminated by R.D. failure but Δ P rose from 175.8 to 632.8 kkgf/m^2 when run was stopped.
24	10.5	1934	335	25.0	140.6	Normal	Good	Good	Smooth with Δ P rising initially to 158.2 kkgf/m^2 and holding constant.

(continued)

TABLE 3 (continued)

Run	Pretreatment pH	Pressure kkgf/m^2	Temperature °C	Black liquor solids %	System[a] ΔP kkgf/m^2	Char appearance	Filtering ability	Cake washing ability	Running ability
25	10.0	1934	340	27.5	158.2	Normal	Good	Good	Run was not terminated by R.D. failure, but ΔP rose from 158.2 to 316.4 kkgf/m^2 when run was stopped.
26	10.0	1776	335	25.0	203.9	Normal	Good	Good	Run was not terminated by R.D. failure, but ΔP had risen to 281.2 kkgf/m^2 when run was stopped.
27	10.0	1776	340	30.0	239.1	Normal	Good	Good	Run was not terminated by R.D. failure, but ΔP had risen to 773.4 kkgf/m^2 when run was stopped.
28	10.0	1934	345	27.5	140.6	Grainy	Moderate	Bad	Run was not terminated by R.D. failure, but ΔP had risen to 667.9 kkgf/m^2 when run was stopped.
29	9.5	1934	340	27.5	123.0	Slightly thixotropic	Good	Good	Smooth with ΔP rising initially to 175.8 kkgf/m^2 and holding constant.
30	10.0	1934	345	25.0	112.5	Slightly grainy	Good	Fair	The run proceeded in moderate fashion with ΔP rising slowly to 281.2 kkgf/m^2 during the run.
31	10.0	1934	340	27.5	123.0	Normal	Good	Good	Smooth with ΔP holding constant at 140.6 kkgf/m^2 after an initial rise to that value.
32	10.0	1934	340	30.0	123.0	Normal	Good	Good	Run was not terminated by R.D. but ΔP had risen to 632.8 kkgf/m^2 when run was stopped.
33	10.0	1934	340	25.0	140.6	Normal	Good	Good	Smooth with ΔP rising initially to 158.2 kkgf/m^2 and holding constant.
34	10.0	2109	340	30.0	140.6	Normal	Good	Good	Run was not terminated by R.D. failure, but ΔP had risen to 808.6 kkgf/m^2 when the run was stopped.
35	10.0	1776	330	27.5	203.9	Normal	Good	Good	The run proceeded in moderate fashion with ΔP rising slowly to 298.8 kkgf/m^2 during the run.

a) This is the pressure drop through the system on water before the run on black liquor was started.

were made within the proven limits of pretreatment and temperature conditions. Seventeen out of the twenty runs produced 10,000 kg of acceptable char from a total of 77,400 liters of black liquor. Yield of char based on black liquor solids was about 23%.

Although this campaign was successful in producing the char required for dry end operation, three out of twenty runs were terminated or hindered by relief disc failure and another eight runs showed large increases in ΔP during operation on black liquor. After Run 20, the system was shut down for mechanical cleaning of the reactor preheater and after Run 27, the reactor was cleaned.

Table 4 shows the distribution of runs according to ease of operation as a function of the operating conditions. It is apparent that reaction temperature is the controlling variable and that temperature preferably should be limited to 330°C for trouble-free operation. As will be seen later, utilization of this information was complicated by an overdesign of the pilot plant equipment.

Dry end operational testing began as soon as char started to come from the wet end. Early results indicated that the sodium content of the char, averaging 1.55% on a dry weight basis, was too high (see discussion of dry end operation). An acceptable level was about 0.5% sodium. Laboratory experiments showed that this level could be reached easily by acid washing the char. All char on hand and all subsequent production was acid washed.

WET END PRODUCTION DEMONSTRATION

Based on the analysis of Runs 1-35, which pointed to reaction temperature as the variable controlling the deposit problem, five Runs (36-40) were made to explore lower temperatures and to retrain the operating personnel before atempting a sustained run. Results of these runs are shown in Table 5. All of these runs proceeded smoothly and produced char which filtered and washed easily. The lowest temperature (320°C) produced a slightly thixotropic char. The five runs processed 19,000 liters of black liquor and produced 2,500 kg of char for dry end operations.

During two earlier runs at 330°C (Runs 17 and 35), it was observed that the temperature control was difficult. The temperature tended to rise above the control point and it was necessary to turn off the reactor preheater occasionally to avoid this increase. This problem became more pronounced during operation at still lower temperatures and the reactor preheater had to be operated in on-off cycles. It became apparent that the reactor preheater had been oversized for the actual heat duty required by the process.

The low temperature runs (36-40) contributed very little to increased ΔP. However, the system contained substantial deposits built up by Runs 28-34, so the system was mechanically cleaned in preparation for sustained operation. The continuous run, Run 41, is listed in Table 5. Average

TABLE 4. EASE OF OPERATION-PRODUCTION RUNS FOR DRY END TESTING

	pH					Pressure kkgf/m^2			Temperature °C				
	11.5	11.0	10.5	10.0	9.5	1776	1934	2109	330	335	340	345	350
Number of runs	1	2	3	25	4	8	26	1	2	11	17	3	1
Percent terminated or hindered by relief disc failure	100	50	0	16	0	25	15	0	0	18	12	33	100
Percent showing large Δ P increase without relief disc failure	0	0	0	36	0	38	19	100	0	18	30	33	0
Percent good operation	0	50	100	48	100	38	66	0	100	64	58	33	0

TABLE 5. WET END PRODUCTION DEMONSTRATION

Run	Pretreatment pH	Pressure kkgf/m^2	Temperature °C	Black liquor solids %	System[a] Δ P kkgf/m^2	Char appearance	Filtering ability	Cake washing ability	Running ability
36	10.0	1776	330	27.5	203.9	Normal	Good	Good	Smooth with Δ P rising initially to 210.9 kkgf/m^2 and holding.
37	10.0	1776	325	30.0	203.9	Normal	Good	Good	Smooth with Δ P having risen to 246.1 kkgf/m^2 when the run was stopped.
38	10.0	1776	320	27.5	246.1	Slightly thixotropic	Good	Good	Smooth with Δ P holding at 228.5 kkgf/m^2.
39	10.0	1776	325	25.0	228.5	Normal	Good	Good	Smooth with Δ P holding at 228.5 kkgf/m^2.
40	10.0	1776	330	25.0	228.5	Normal	Good	Good	Smooth with Δ P holding constant at 228.5 kkgf/m^2.
41	10.0	1776	330	27.5	52.7	Normal	Good	Good	This was the continuous run demonstration. The run proceeded smoothly for most part with the Δ P increasing slowly during run. The run was terminated after 27 hours by R.D. failure. The Δ P had increased to 984.3 kkgf/m^2 when R.D. failed.

a) This is the pressure drop through the system on water before the run on black liquor was started.

conditions were 10.0 pH, 1776 kkgf/m^2, and 330°C. The char product was normal in appearance and filtered and washed easily. Operation generally was smooth but there was a gradual increase in ΔP culminating in relief disc failure after 27 hours of operation. It was most difficult to control the reaction temperature at 330°C and the temperature climbed above this level whenever the reactor preheater was on. Each time this happened, the system ΔP increased. If there had been a way to avoid the temperature surges, it is believed that the run could have continued indefinitely.

The continuous run processed 67,500 liters of black liquor and produced 8,700 kg of char, a yield of about 23.3% based on black liquor solids.

ADDITIONAL PRODUCTION RUNS

The char produced through and including Run 41 was insufficient to supply the planned dry end operating schedule. A series of fourteen runs, Runs 42-55, was required to produce the additional char. Results are summarized in Table 6.

After the 27 hour run (Run 41) the system had a high ΔP, i.e. bad deposits. The reactor was cleaned to reduce the deposits, but when operation was resumed the ΔP still was quite high and it became apparent that the reactor preheater also was dirty. Operation was smooth but somewhat cumbersome. After Run 47, the system was given a complete cleaning to simplify operation. This series of runs provided an opportunity to check the conclusion that excessive reaction temperature was the cause for deposits. While the reactor was being cleaned prior to Run 42, the cross exchanger was modified to throw more heat duty into the reactor preheater and bring its load within a range which could be controlled. During Runs 42-55, temperature never was allowed to rise higher than 330°C and several lower temperatures were investigated. As can be seen in Table 6, increases in ΔP were minimal during this series of fourteen runs and there were no relief disc failures nor threats of failures. The amount of black liquor processed was 96,400 liters, and 14,100 kg of char was produced, giving a yield of about 26.1% based on black liquor solids. This production was about one and one-half times the production during the 27 hour continuous run.

The information and observations developed during this series of fifty-five runs convincingly relates the deposit (plugging) problem to the control of reaction temperature. With an adiabatic tubular reactor configuration, such as the pilot plant reactor, relatively low temperature is required to avoid rapid formation of char in a localized area. With other reactor configurations designed to distribute the reaction over a larger area, higher operating temperatures should be feasible.

The true effect of temperature was difficult to detect in the pilot plant because temperature control deteriorated as the temperature was reduced. The control problem resulted from greater than expected efficiency of heat transfer in the cross exchanger and from the exothermal heat of reaction which was not recognized in smaller scale work. Thus, the heat input required from the reactor preheater was reduced by the higher temperature entering the preheater and was further reduced by the exotherm. As

TABLE 6. ADDITIONAL WET END PRODUCTION RUNS

Run	Pretreatment pH	Pressure $kkgf/m^2$	Temperature °C	Black liquor solids %	System ΔP $kkgf/m^2$	Char appearance	Filtering ability	Cake washing ability	Running ability
42	10.0	1758	330	30.0	246.1	Normal	Good	Good	Smooth with ΔP rising slowly to 351.6 $kkgf/m^2$.
43	10.5	1758	320	30.0	298.8	Normal	Good	Good	Smooth with ΔP rising initially to 351.6 $kkgf/m^2$ and holding constant.
44	10.0	1758	320	30.0	281.2	Normal	Good	Good	Smooth with ΔP rising initially to 369.1 $kkgf/m^2$ and holding constant.
45	10.5	1758	315	30.0	351.6	Normal	Good	Good	Smooth with ΔP rising initially to 386.7 $kkgf/m^2$ and holding constant.
46	10.5	1758	325	30.0	351.6	Normal	Good	Good	Smooth with ΔP rising slowly to 509.7 $kkgf/m^2$.
47	10.5	1758	330	30.0	246.1	Normal	Good	Good	Smooth with ΔP rising slowly to 421.9 $kkgf/m^2$ and holding constant.
48	10.0	1758	330	25.0	35.2	Normal	Good	Good	Smooth with ΔP rising initially to 52.7 $kkgf/m^2$ and holding constant.
49	10.0	1758	320	32.5	52.7	Normal	Good	Good	Smooth with ΔP rising initially to 87.9 $kkgf/m^2$ and holding constant.
50	10.0	1758	330	27.5	52.7	Normal	Good	Good	Smooth with ΔP rising initially to 87.9 $kkgf/m^2$ and holding constant.
51	10.0	1758	320	20.0	70.3	Normal	Good	Good	Smooth with ΔP rising initially to 87.9 $kkgf/m^2$ and holding constant.
52	10.0	1758	320	27.5	87.9	Normal	Good	Good	Smooth with ΔP rising initially to 105.5 $kkgf/m^2$ and holding constant.
53	10.0	1758	310	25.0	105.5	Normal	Good	Good	Smooth with ΔP holding steady at 123.0 $kkgf/m^2$.
54	10.0	1758	310	25.0	105.5	Normal	Good	Good	Smooth with ΔP rising initially to 123.0 $kkgf/m^2$ and holding steady.
55	10.0	1758	310	20.0	105.5	Normal	Good	Good	Smooth with ΔP rising initially to 123.0 $kkgf/m^2$ and holding steady.

the temperature control point was decreased, the demand on the preheater became so low that the input could not be controlled. Although reducing the temperature alleviated deposits in the reactor, the surges brought on by control problems caused too much reaction to occur in the preheater and created deposits there.

The relative freedom from deposits in the later stages of this campaign demonstrate that the process can be operated free of deposit problems by proper thermal sizing of heat recovery, heating, and reaction equipment and by close control of temperature at the stage where the reaction is proceeding rapidly.

Table 7 is an amplification of Table 4 to include all fifty-five runs and clearly shows the critical role of temperature.

Table 7. EFFECT OF TEMPERATURE ON PLUGGING

Temperature °C	Percent of runs with little or no plugging
310	100
315	100
320	100
325	100
330	100
335	64
340	59
345	33
350	0

DRY END OPERATIONS

Analysis of Pilot Plant Char

In Section V, the nature of hydropyrolysis char produced on a laboratory scale was discussed. To relate the properties of pilot plant char to the laboratory char, representative pilot plant chars were analyzed by an independent testing laboratory. Proximate analysis, ultimate analysis, and fusion temperature of the ash were determined on char which had been acid washed and dried.

PROXIMATE ANALYSIS OF PILOT PLANT CHAR
(percent)

	As received	Dry basis
Moisture	7.71	-
Ash	2.82	3.06
Volatile	32.71	35.44
Fixed carbon	56.76	61.50

ULTIMATE ANALYSIS OF PILOT PLANT CHAR
(percent)

	As received	Dry basis
Moisture	7.71	-
Carbon	72.31	78.35
Hydrogen	4.49	4.87
Nitrogen	0.22	0.24
Oxygen	10.81	11.70
Sulfur	1.62	1.76
Chlorine	0.02	0.02
Ash	2.82	3.06

FUSION TEMPERATURE OF ASH
(°C)

	Reducing atmosphere	Oxidizing atmosphere
Initial deformation	882	888
Softening (H=W)[a]	904	954
Softening (H=1/2W)	921	982
Fluid	960	1038

[a]H is cone height, W is cone width

The data show that pilot plant char contained less carbon and more hydrogen than the laboratory char and the coals described in Section V. Considering the adjustments in hydropyrolysis conditions which were required between the laboratory and pilot operations, some change in char properties would be expected. Volatile matter, the most important factor, was within the acceptable range for production of good activated carbons. Fusion temperatures of the ash indicated that slagging should not be a problem at calcination (600° to 750°C) and activation (750° to 850°C) temperatures appropriate for hydropyrolysis char.

Drying Operations

As noted in the pilot plant description, the pilot plant dryer is a batch unit selected to serve as a tool for drying the char. It was not expected to provide design data adequate for commercial equipment selection. It did provide data to simplify later trials on continuous equipment at vendor facilities.

Proper dryer charge was found to be 91 to 136 kg wet filter cake at 40% to 60% solids. As mentioned in the equipment description, the dryer could tolerate 87.9 $kkgf/m^2$ (125 psig) pressure at 343°C. Unfortunately, this steam pressure and temperature develops a drying rate (vapor load) far in excess of the capability of the condenser/receiver system, flooding the vacuum pump. Good operation was obtained at a steam pressure of 4.2 $kkgf/m^2$ (6 psig).

Table 8 gives drying rate data for a variety of loads, temperatures, and vacuum levels. Comparing Run 3 to Run 4 and Run 8 to Run 9, the effect of changes in vacuum at constant temperature is shown. Runs 1, 5, and 6 utilized the same temperature and vacuum levels but the char load in the dryer was varied from 54 kg to 159 kg. It was mentioned earlier that operation at high temperatures would cause a vapor removal rate high enough to flood the vacuum pump. In Run 7, initial drying was done with the system open to atmosphere, then vacuum was used after the maximum vapor load was passed. Although this did alleviate the flooding problem, the drying rate without vacuum was too slow, and use of higher temperatures to increase the drying rate, with the system exposed to air, would risk combustion of the char.

As noted earlier, hydropyrolysis char has a chemical reactivity greater than coal. This reactivity, although an advantage during the activation step, gives the char pyroforic properties, i.e. the heat of adsorption of oxygen from air raises the temperature to the ignition level. Laboratory data indicate that the maximum temperature at which hydropyrolysis char can be exposed to air is 50°C. Thus, although the char is processed at temperatures above 50°C, it must be cooled to or below this temperature before discharge and exposure to air.

Continuous Dryer Trial--

To obtain data for commercial design, acid washed char filter cake was dried in vendor facilities using a LUWA D-210 continuous dryer operating on the thin film principle. At a steam heating pressure of 105.5 $kkgf/m^2$ (150 psig), char was dried to 5% to 7% moisture at product rates of 34 to 41 $kg/hr/m^2$ of heated surface. Performance under vacuum up to 300 mm Hg was not enough better than atmospheric operation to justify the added capital and the greater difficulty of feeding wet cake into a vacuum. As noted earlier, steps to exclude air would be required.

The product was a good powder. The only problem experienced was bridging of the wet filter cake in the dryer feed hopper. A positive feeding system is required rather than simple gravity flow.

Table 8 DRYING RATES

Run[b]	Load, kg	Shell temperature, °C	Absolute vacuum, mm Hg	Initial moisture, %	Time to 10% moisture, min	Time to 5% moisture, min
1	Standard (91-113 kg)	106	150	47	167	188
3	Standard	102	50	34	212	240
4	Standard	102	200	33	95	122
5	Standard	106	150	36.5	126	139
6	159 kg	106	150	35.5	150	170
7	Approx. 54 kg	111	0-200[a]	41.5	235	255
8	Standard	111	200	48	103	128
9	Standard	111	100	36.5	83	98

[a]Initial drying with no vacuum.

[b]Run 2 is not tabulated due to equipment malfunction.

Compacting Operations

In the original concept, this grant program visualized treatment of effluent with a powdered carbon and use of the loaded carbon as fuel after one adsorption. Part I of the program soon showed that the economics favored a granular carbon which would be regenerated thermally between loadings. Hydropyrolysis char typically is a uniformly fine material. Under some wet end operating conditions, a somewhat coarser product was obtained.

SCREEN ANALYSIS OF DRY CHAR
(weight percent)

Sieve fraction	Typical product	Coarse product
+35 mesh	2.7	0.3
-35 + 60	1.7	0.0
-60 + 120	1.0	3.8
-120 + 200	2.8	31.4
-200 + 325	29.1	32.0
-325 mesh	62.8	32.5

There are a number of methods used commercially to convert a powder into a granular material. Among these are compaction, agglomeration, and extrusion. Usually, a binder material is added to strengthen the granules. Based on inquiries and evaluation of existing technology, it was judged that the compaction method using a roll press would be the best selection for hydropyrolysis char.

Strength (hardness) is an important property of granular carbons, which must have sufficient strength to withstand the production steps of calcination and activation and repeated regenerations with minimum attrition and breakage. Hardness can be evaluated by a destructive testing procedure in which a dry sample is shaken for 3 hours on a reinforced 60-mesh screen with steel balls. The percentage of the granules surviving in the original size range is a measure of hardness. Relatively speaking, the greater percent survival, the stronger the carbon.

To study compacting variables, the pilot equipment was operated initially to produce small (100 to 200 kg) quantities of compacted char. This is about one hour of compactor operation. Later as additional expertise was developed, sufficient material was processed for multiple hearth furnace operation.

Effect of Binder Type--

In general, coal tar pitch is considered to be a good binder for carbons which must be subjected to high temperature conditions and retain their strength. One way to classify this binder is according to melting point. It was believed initially that the use of pitches of different melting points might vary product quality. By lowering the melting point, the binder might become more tacky or even flow when subjected to the frictional heat of the compactor. This effect could enhance strength by causing better adhesion. A second, and possibly a counteracting effect, is the increase in binder carbon content with increasing melting point. It would be expected that the higher the carbon content the stronger would be the binder structure after calcination.

To evaluate this variable, binders in the melting point range of 98° to 143°C were used and the compacted products were activated and hardness tested. Within the experimental error of the testing, no change in product strength could be attributed to change in binder melting points. The 143°C melting point binder was chosen for future pilot operation as it was available commercially in a pulverized form. This binder is designated as No. 1 Ebony core binder without cereal binder or oil.

Effect of Binder Amount--

Hydropyrolysis char was compacted using no pitch binder, 5% binder and 10% binder. The three compacted and granulated products were calcined for 1 hour in the multiple hearth furnace at 650° to 700°C. The calcined products were tested for hardness and compared to a commercial granular activated carbon.

HARDNESS AFTER CALCINING
(Percent retained in original 16x20 mesh range)

Product	Hardness
Char, no binder	77
Char, 5% binder	85
Char, 10% binder	84
Commercial activated carbon	69

These results indicated that compacted and calcined hydropyrolysis char should resist attrition during activation. The data do not show that hydropyrolysis activated carbon will be stronger than commercial activated carbon because strength normally decreases during the activation step. The data show that binder addition above 5% probably would not significantly increase strength. Further testing to determine optimum binder addition was not conducted. In fact, it was felt that no added binder would be needed but the decision was made to use binder as insurance in subsequent operations.

Effect of Char Moisture Content--

A series of compaction runs was made varying the char moisture content. The char contained 5% binder. Equipment operation was observed and the products were calcined and tested for hardness. The results are shown in Figure 22. There are four zones of operation:

Zone 1: moisture 2% and below - The char is too dry for the feed screw to grab the material and predensify it for the roll press. The char simply flows through the feed screw and rolls with no compaction.

Zone 2: moisture 2% to 8% - This is the operable range for the equipment. As moisture increases above 2%, frictional forces in the feed screw increase and heat is generated, causing softening of the binder. Product quality increases to a maximum at about 8% moisture.

Zone 3: transition at 8% moisture - Operation is unstable. Product quality varies from very good when the system can operate, to poor when the feed screw lacks the power to predensify the char. The transition at about 8% moisture is abrupt; to allow a margin for errors, safe operating range was set at 6% to 7.3% moisture.

Zone 4: moisture above 8% - The feed screw locks up and the compactor can only be operated intermittently. The rolls do not have time to heat up and the system does not reach steady state. Quality is consistently poor during the brief intervals when anything is produced.

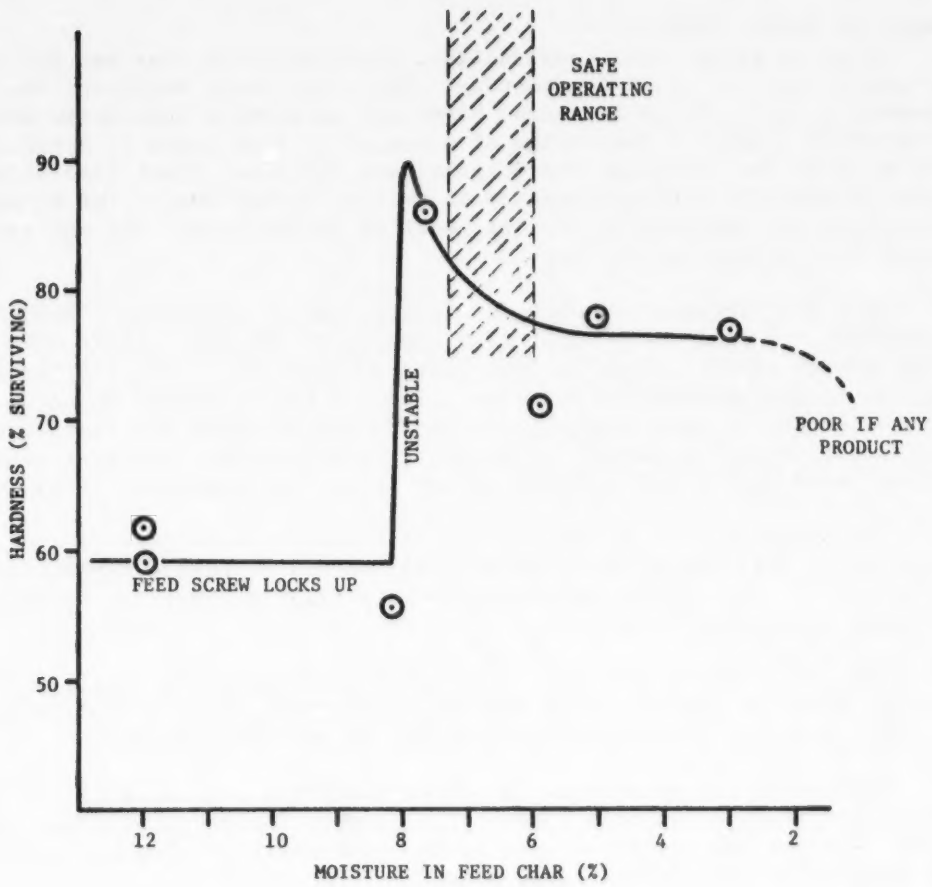


Figure 22. Effect of moisture content on hardness of compacted char.

Material Balance--

After establishing acceptable conditions of 5% binder, 6% to 7.3% moisture, and a feed rate of 135 kg/hr, compactor operation was standardized at these conditions and, thereafter, the compactor simply became a tool to prepare material for multiple hearth furnace operations. During the later operating periods, a material balance was made around the compaction system for commercial design purposes. The balance is shown in Figure 23.

Compactor Vendor Tests--

Prior to pilot plant construction, hydropyrolysis char was not available in quantities sufficient for testing. The pilot plant compactor was designed assuming a feed similar to carbon black and included a feed screw with diminishing flights. The design of a compactor feed screw is particularly sensitive to the nature of the material and the pilot plant feed screw jammed frequently during operation on hydropyrolysis char. The screw was compacting the material beyond the point of squeezing out air and became packed full of compressed char.

When char became available, tests were run in vendor (K-G Industries) facilities. A feed screw similar to the one in the pilot plant unit was tried but no product could be made owing to bridging in the K-G hopper and failure of the material to fill the screw. A high compression screw was then tried but it developed high loads and the material was compacted in the screw; the screw jammed owing to over-compression. The best product was obtained when a uniform-flight feed screw (no compression) was used.

The major problem during this testing was the slow free flow of the material to fill the screw. The material should be pushed mechanically into the screw, or the screw should have more flights above the feeder insert to allow time for filling.

The vendor tests and pilot plant operating experience indicated that some moisture in the char will improve feeding behavior and reduce dusting. Too much moisture will aggravate bridging in the feed hopper.

During the compactor runs in vendor facilities, granulator knife speed was investigated on a KG 8-6 granulator. The granulator was operated at 300, 600, and 900 rpm knife speeds. The best particle size distribution was obtained at the intermediate speed.

Multiple Hearth Furnace Operations

Initial operation of the multiple hearth furnace utilized a compacted coal in order to conserve the supply of hydropyrolysis char. During this shakedown period, operators were trained and equipment was debugged. The first run on compacted hydropyrolysis char indicated that physical equipment changes were required to handle this material and the modifications were made.

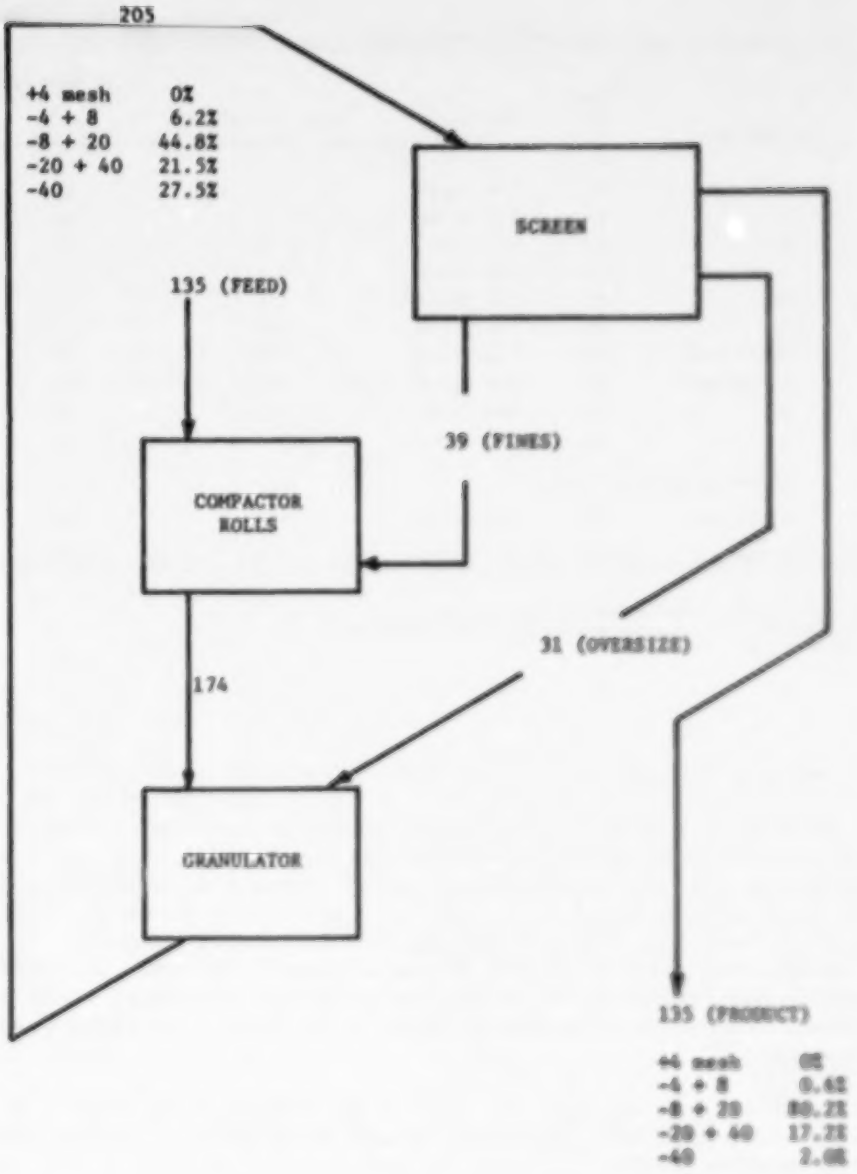


Figure 23. Compactor material balance.

The first useful product data came from Run 2. Data from Runs 2 through 6 are shown in Table 9.

Table 9. MULTIPLE HEARTH RUNS

Run	Condition	Gas temp °C	Residence time	Steam injection rate kg. steam/kg carbon feed	Nitrogen surface area m^2/gm Product	Upper hearths
2	1	832	6 hr 1 min	0	450	HTH=340
	2	873	4 hr 11 min	0	340	" 470
	3	927	4 hr 5 min	0	360	" 260
	4	979	2 hr 58 min	0	230	" 340
	5	875	5 hr 30 min	0	470	" 430
	6	904	3 hr 30 min	0	400	" 240
	7(calc.feed)	876	4 hr 58 min	0	520	" 670
3	1(calc.feed)	819	5 hr 29 min	4 to 5	690	" 610
	2 " "	873	5 hr 29 min	4 to 5	720	" 870
	3 " "	943	5 hr 33 min	4 to 5	500	" 540
4	Calcination only for run 6					
5	1(calc.feed)	886	4 hr 57 min	2	560	HTH=750
6	Average	849	2 hr 33 min	2	508	HTH=778*

*This average includes carbon produced during the final hours using an off-grade feed. Samples earlier in the run typically showed areas of 600 to 660 m^2/gm.

Previous laboratory work had demonstrated that hydropyrolysis char should be calcined before activation. Since the operation of the multiple hearth furnace is similar for calcination and activation, although chemically the processes are different, it was thought that calcination and activation could be accomplished simultaneously in a single furnace. That is, calcination would take place on the upper hearths and activation on the lower hearths. Using a variety of conditions, this concept was tried in Run 2 and failed to produce satisfactory carbon. Discussion with the furnace manufacturers indicated that separate calcining would be beneficial. Condition 7 in Run 2, using a previously calcined feed, confirmed this.

A calcining run was made to prepare material for activation in Run 5. Sample analyses from the calcining run are shown below. Conditions were 1 hour at 649° to 704°C.

CALCINING
(Percent volatile in product)

Sample	Volatile
Feed	33.9
Hearth 1	23.3
Hearth 2	5.3
Hearth 3	5.6
Hearth 4	5.2
Hearth 5	5.9
Hearth 6	5.6
Product	5.9

The apparent differences beyond hearth 2 are within sampling error. Devolatilization takes place on hearths 1 and 2, but it is known that time at temperature beyond devolatilization aids in setting the carbon structure and is beneficial. Therefore, the 1 hour calcination time was adopted for all future calcinations.

During Run 3 on calcined char, the furnace burners operated poorly and control was difficult but good activated carbon was produced. This carbon was categorized and compared with two commercial carbons, with the results shown in Tables 10 and 11.

Table 10. CATEGORIZATION OF ST. REGIS ACTIVATED CARBON, PITTSBURGH CAL AND GRANULAR DARCO

Carbon	N_2 Surface area m^2/gm	Apparent[1] density g/cc	% Ash D.W.B.	CCl_4 No.	Iodine No.	Hardness Mgr. % surviving test -10+20 mesh	-20+25 mesh
St. Regis	720	.44	0.1	49	1148	80	84
Pittsburgh CAL	1040	.43	0.1	79	1266	86	--
Granular Darco	760	.47	14.5	50	632	--	48

[1] Wrapped density

[2] Granular Darco was not available in -10+20 mesh size.

Table 11. LOADING COMPARISON OF ACTIVATED CARBONS[1]

	St. Regis Carbon			Pittsburgh CAL			DARCO Granular		
Color concentration, cu	1000	500	100	1000	500	100	1000	500	100
Color loading, cu/g	250	190	100	170	34	<10	220	150	85
Ratio STR/CAL	1.47	5.6	>10						
STR/DARCO	1.14	1.27	1.18						
TOC concentration, mg/l	160	100	70	160	100	70	160	100	70
TOC loading, mg/g	150	40	16	120	27	16	45	25	17
Ratio STR/CAL	1.25	1.5	1.0						
STR/DARCO	3.3	1.6	1.0						
BOD concentration, mg/l	120	90		120	90		120	90	
BOD loading, mg/g	~20	<1		9	6		16	6	
Ratio STR/CAL	2.2	<0.17							
STR/DARCO	1.2	<0.17							

1. Isotherms were run on 0.05% Black Liquor simulated effluent as mill upsets prevented obtaining typical mill effluents. APHA Standard Method used.

The data showed that activated hydropyrolysis char is competitive with the commercial carbons. Hardness of the hydropyrolysis product appeared to be better than the commercial products. Isotherm tests showed performance levels which established that hydropyrolysis char can be activated to acceptable quality for effluent treatment.

After Run 3, furnace modifications and repairs were made to provide better operation. Run 4 was a production run to calcine sufficient char for a sustained demonstration of activation. Run 5 was a short activation run to check the effects of the modifications made to the furnace system. Hearth 3 showed higher activation than the final product, indicating that retention time should be shortened.

Run 6 constituted the final demonstration of activated carbon production. Production was sustained for 96 hours and all available char was processed. Maximum activation again was reached on hearth 3, indicating that shorter (1 hour) retention time would have produced a better final product. The increase in activation rate experienced during Runs 5 and 6 is attributed to improved furnace operation and control.

SECTION X

ACTIVATED CARBON PLANT DESIGN AND COST ESTIMATE

OVERALL DESIGN CRITERIA

Engineering design studies were made for the sizing of four different plants that would be capable of producing activated carbon. The microlime-carbon method for treatment of unbleached kraft effluent, as outlined in a previous EPA report prepared by St. Regis (2), was used as the basis on which the activated carbon plants were designed. The four plants were sized to produce the makeup requirements for one, two, three, and four such microlime-carbon treatment facilities.

An engineering design study was conducted independently by St. Regis for an approximately 330 ton/day pulp equivalent hydropyrolysis plant. Results indicated a cost of $17.9 million in May 1975 dollars. It is obvious that a hydropyrolysis system could not be justified economically on the basis of activated carbon production. The justification for a hydropyrolysis plant must be based on recovery of pulping chemicals and energy. In this study, it was assumed that a hydropyrolysis facility would be present and that a fraction of the total char sufficient to feed the carbon activation plant would be available. The energy content of the char is 7500 cal/kg. Char is charged to the activated carbon plant at its fuel value.

DESIGN METHODS AND ASSUMPTIONS

A flow diagram for the roposed activated carbon plant is given in Figure 24. This flow diagram shows the major pieces of equipment that are used in the process. They are as follows:

dry char storage

compactor

compacted char storage

multiple hearth furnace

calcined char storage

activated carbon storage

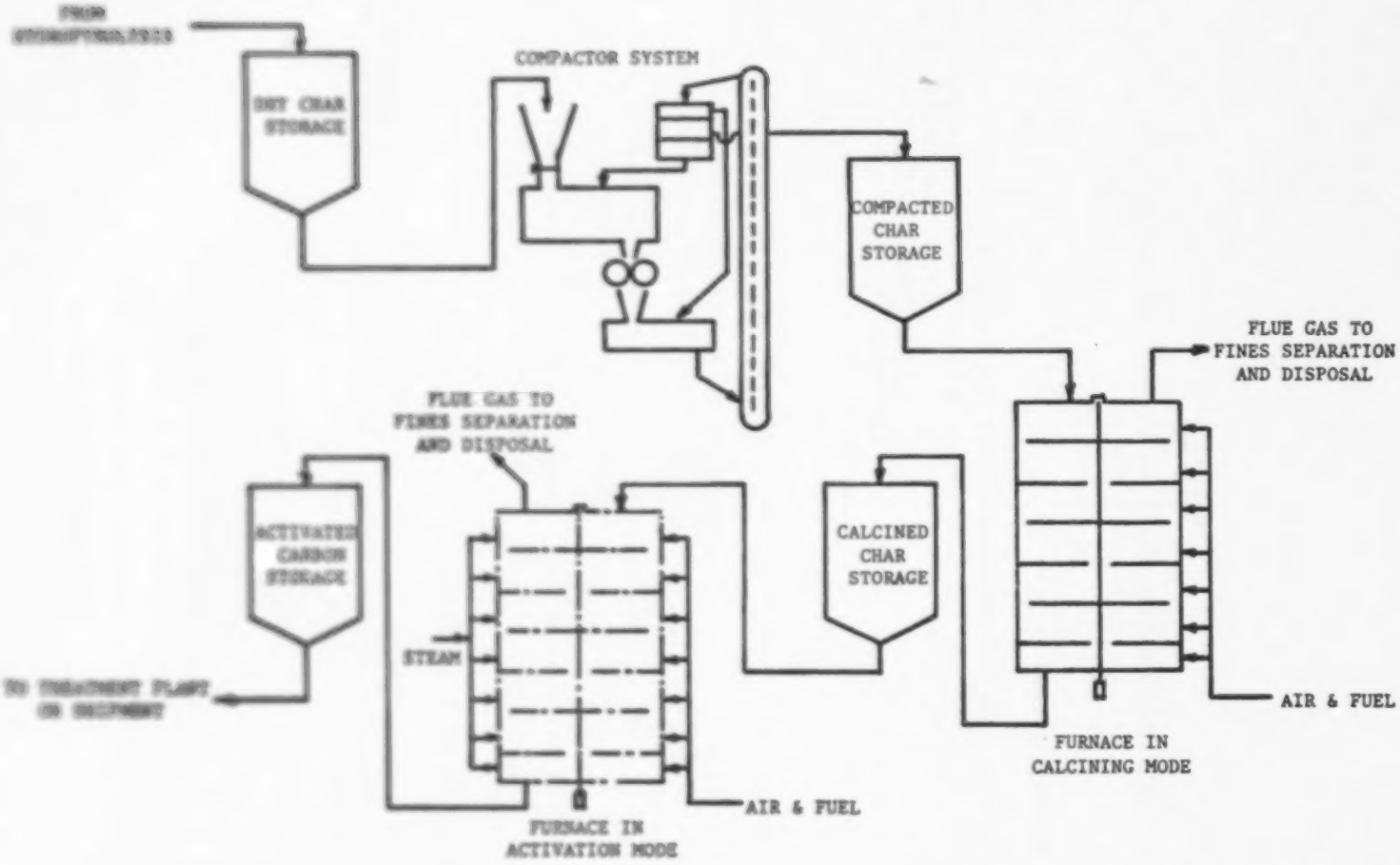


Figure 24. Carbon activation flow diagram.

The storage bins are sized to provide a certain hold up time, which varies from bin to bin according to the solid material to be stored. However, since the cost of a bin is directly related to the volume of material it can hold, the size of the bins is referred to their capacity in cubic meters. The bulk density of the material to be stored in the bin is used to convert the hold-up time into a volumetric capacity. The bulk densities for the materials involved in the plant are:

Material	Bulk density, kg/m^3
Compacted Carbon	708
Regenerated Carbon	400
Calcined Carbon	634
Activated Carbon	500

The bins are constructed of carbon steel and have 30° tangent to tangent conical bottoms.

The compactor is sized to generate a certain capacity in kg/hr of -7+20 mesh product. The equipment combines the operations of mixing, compaction, granulation, and screening into one unit. The operation of binder blending is not included. In pilot compactor operations (see Section IX), it was noted that binder probably would not be needed, but 5% coal tar pitch was added for insurance. After activation, the carbons were harder than commercial carbons, which strengthened the opinion that no added binder was needed.

The calcination and activation operations are performed in the multiple hearth furnace. The furnace is equipped with a belt feeder and rotary-lock inlet valve for the solids. The rabble arm shaft is air cooled, as are the rabble arms. Capability for steam injection on each hearth is provided. The assembly for the treatment of combustion off-gases consists of an afterburner, scrubber, and discharge stack. A cooler is provided at the furnace discharge for the purpose of reducing the carbon product temperature. The design rates for activation and calcination are 2.44 $kg/m^2/hr$ and 34.18 $kg/m^2/hr$, respectively. The calcination rate is based directly on pilot plant results; activation rate is extrapolated from pilot plant operating data.

Material handling in the plant is accomplished primarily by belt conveyors and bucket elevators. The use of screw conveyors is avoided, since they cause attrition in the carbon product.

Since the operations of calcination, activation, and regeneration all are carried out in a multiple hearth furnace, there exists the possibility of process economy by combining some of these operations. Clearly, three different approaches can be taken: 1) Each operation can have its own furnace. 2) The calcination and activation operations can be scheduled into one furnace and regeneration performed in another. 3) All three

operations can be scheduled into the same furnace. In approaches one and two, the regeneration furnace would be included in the treatment facility. However, in approach three the furnace would be located in the activation facility. This means that the regeneration operation would have to be separated from the treatment system. Certain complications immediately arise because of this. Firstly, the cost of the furnace must be divided between the activated carbon plant and the effluent treatment plant. Secondly, the furnace operating time must be divided between calcining, activating, and regenerating. Approach number one is the simplest in terms of design. But approaches two and three could be more economical and, of course, the most economical design should be selected.

For sizing the regeneration furnace, a rate of 7.32 $kg/m^2/hr$ is used based on data developed in a previous report (2). Also from that report, the carbon dosage rate for the microlime-carbon effluent treatment plant is 453.6 kg/hr. The expected loss per regeneration cycle is 10%, so the fresh carbon make-up rate is 45.4 kg/hr.

The cost of activated carbon should be reduced by increasing the production rate. To do so would require that the activation plant supply carbon to more than one effluent treatment facility or that the surplus be sold. Design calculations were made for carbon activation plants supplying make-up carbon to two, three, and four microlime-carbon treatment systems, i.e. rates of 90.8, 136.2, and 181.6 kg/hr.

COST ESTIMATES

Cost estimates were prepared for the activated carbon facilities discussed above. The purpose in making these various estimates was to select the plant design which yields the lowest cost carbon. These estimates are believed to be within ± 30% of the actual costs. The bases for the estimates were the same as those used in the plant designs. All cost figures are reported in October 1975 dollars.

The capital costs for the activated carbon plants were based on a confidential study on an activated carbon system prepared for St. Regis. The capital cost for each plant was derived by estimating the costs of the major pieces of equipment - storage bins, compactor, multiple hearth furnace - and then applying a factor to scale up to the total plant cost. The costs of the storage bins, compactor, and activation furnace were estimated from quotes received during the last six months. The costs of the regeneration system were estimated from the data of Hutchins (13) and a confidential study prepared for St. Regis.

The bases for determining the operating expenses were as follows:

Fixed Expenses

Salaried Personnel - 0.4 man at $16,000/man yr.

Salary expense - 10% of salary

Amortization - 6.25% of total cost of investment (TCI) per year.

Insurance and taxes - 2% TCI/yr.

Semi-Variable Expenses

Repairs and maintenance - 5% TCI/yr

Telephone and telegraph - 8% of salary

Travel - 15% of salary

Variable Expenses

Operating labor - 1.5 people per shift at $7.05/hr

Payroll expense - 20% of operating labor

Operating supplies - calculated directly

Fuel - $7.94/million kg-cal

Purchased power - $0.03/kwh

Steam - $4.52/1000 kg

Basic raw material - hydropyrolysis char at its fuel value

For the production of activated carbon the following utility requirements must be met:

Fuel - 9300 kg cal/kg of activated carbon

Steam - 4 kg steam/kg of activated carbon

Purchased power - 0.1014 kwh/kg of activated carbon

Results of Cost Estimates

Capital and operating costs are shown in Table 12. In each estimate, the capital costs are listed for both the activation facilities and the regeneration facilities. The cost of the regeneration facility is absorbed into the effluent treatment plant and does not enter into the operating cost for the production of activated carbon. It is given for the purpose of showing how the various plant designs influence the regeneration cost.

TABLE 12. COST ESTIMATES FOR ACTIVATION PLANTS

Estimate number	1	2	3	4	5	6
New carbon production (kg/hr)	45.4	45.4	45.4	90.8	136.2	181.6
Regenerated carbon production (kg/hr)	408.2	408.2	408.2	408.2	408.2	408.2
Capital cost ($ million)						
Total	8.110	5.625	4.315	4.755	5.165	5.600
Allocated to regeneration	2.180	2.180	1.695	1.415	1.140	1.000
Allocated to calcination and activation	5.930	3.445	2.620	3.340	4.025	4.600
Operating expenses ($/kg of activated carbon)						
Fixed			0.614	0.389	0.312	0.266
Semi-variable			0.364	0.232	0.186	0.159
Variable			0.544	0.638	0.600	0.544
Total			1.522	1.259	1.098	0.969

Estimates 1, 2 and 3 deal with plants which are capable of producing the make-up activated carbon and meeting the carbon regeneration requirements for one microlime-carbon treatment facility operating at a carbon dosage rate of 453.6 kg/hr. Estimate 1 considers a plant with the operations of calcination, activation, and regeneration being carried out in three separate furnaces. Estimate 2 considers a plant with calcination and activation scheduled into one furnace and regeneration carried out in a separate furnace. Estimate 3 considers a plant with calcination, activation, and regeneration scheduled into a single furnace. It is apparent that the design with all three functions scheduled into one furnace yields the lowest costs. The other two alternatives were eliminated from any further consideration.

Estimates 4, 5, and 6 deal with larger plants capable of producing the make-up activated carbon for two, three, and four microlime-carbon effluent treatment facilities. Each estimate used the design where calcination, activation, and regeneration were scheduled into one furnace. The regenerated carbon production was that needed by one (local) treatment plant. In each case, scheduling of the three functions was optimized using a computor program and the lowest overall operating cost was selected. Costs were allocated to carbon production and regeneration on the basis of the time fractions of furnace utilization.

As one goes from Estimate 3 to 4 to 5 to 6, it is seen that the capital cost for the activation facility increases. This is expected since the activated carbon production is increasing. The capital cost for regeneration decreases (see p. 80). As the plant size increases, reductions in fixed and semi-variable expenses per unit of production significantly reduce the cost of activated carbon. This is partially offset by the packaging and shipping costs (variable expense) for moving carbon from the larger plants to other using locations.

Conclusions from the Cost Estimates

Figure 25 is a plot of activated carbon cost versus plant capacities considered in this study.

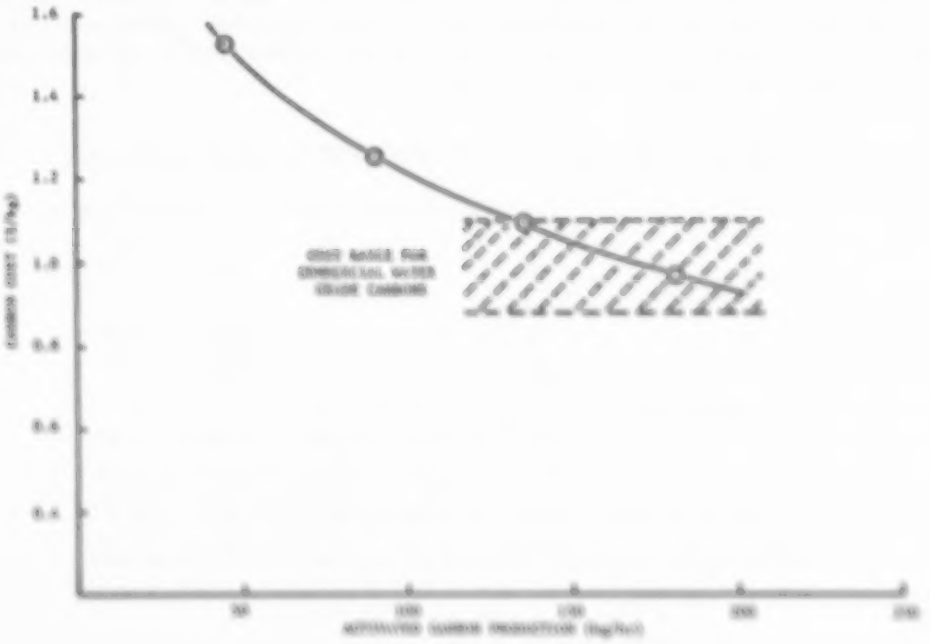
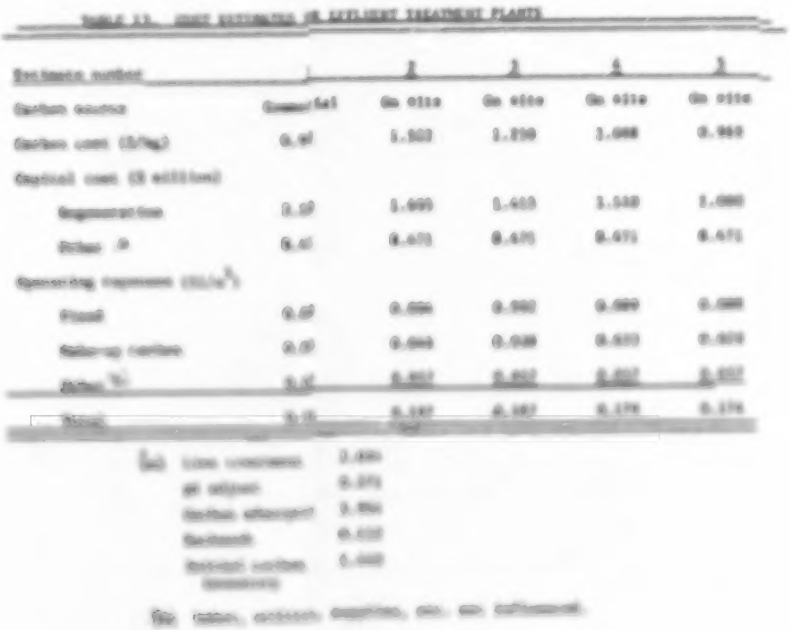


Figure 25. Effect of production rate on cost of carbon.

The shaded area in Figure 25 shows the cost range for commercial water grade activated carbons, i.e. $1.10/kg to $0.88/kg. It becomes obvious that one could buy make-up carbon from commercial sources at a cost no higher than it could be made on site from hydropyrolysis char in the plants considered here.. However, if one has more than the equivalent of four treatment plants of the size that has been dealt with here and wishes to produce the make-up carbon for all these plants at one site, then the carbon could be produced at a lower cost than commercial carbons. The chances of this happening are remote. It is apparent that in order to produce an activated carbon from hydropyrolysis char at a significantly lower cost than commercial carbons, one would have to build a plant comparable in size to most commercial carbon production plants. In other words, one would have to be planning on getting into the activated carbon business.

Effect on Effluent Treatment Costs

The results in Table 12 showed that the capital cost for carbon regeneration could be decreased through association with the process of producing on-site activated carbon. This influences the cost of effluent treatment. As the basis for comparison, consider the same microlime-carbon treatment plant that has been used throughout this study. The costs for this effluent treatment plant in January 1973 dollars have been estimated in some detail in a previous EPA report made by St. Regis (2). The same procedure used for developing costs in that report is used here. Table 13 shows the development of microlime-carbon treatment costs when five different sources of activated carbon are used. These costs are in October 1975 dollars and they do not include any credit for water reuse.



Estimate 1 develops the treatment costs when commercial carbon at a price of $0.99/kg is used as the carbon make-up source. Estimates 2 thru 5 develop the treatment costs when the carbon is made on site at the four different plants considered in Estimates 3, 4, 5, and 6 of Table 12. By comparing Estimates 2 thru 5 with Estimate 1, it can be seen that the use of activated carbon produced on site from hydropyrolysis char can result in a lower treatment cost when compared with the use of a commercial carbon. Figure 26 shows the operating cost of the treatment plant using on-site produced activated carbon plotted versus the production capacity of the activated carbon plant used to generate the make-up carbon. The shaded portion shows the operating cost range of the treatment facility if commercial carbon is used as the make-up source. This again clearly shows that an effluent treatment facility can be operated at a lower cost if on-site produced activated carbon is used instead of commercial sources. Of course, for the cost to be lower one must be producing the make-up activated carbon at one location for use in the equivalent of three or more microlime-carbon treatment plants each with a capacity of 3785 m^3 of effluent per day.

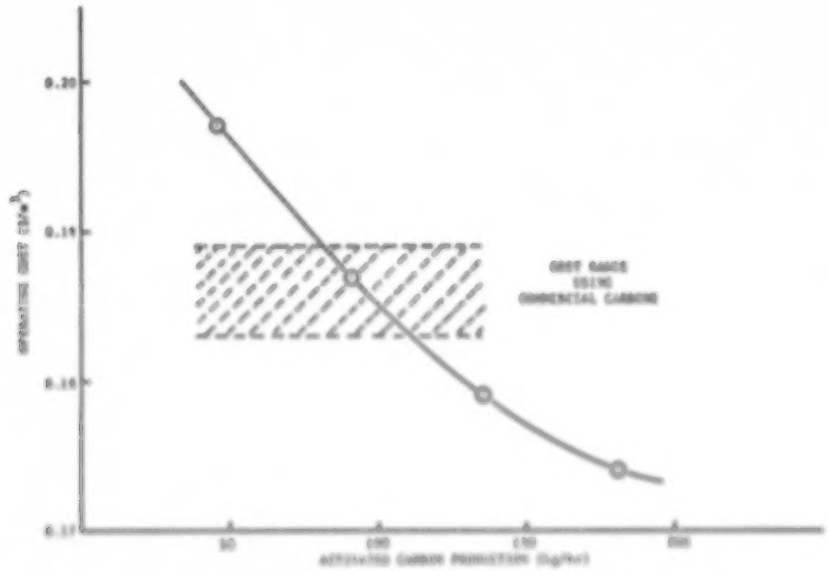


Figure 26. Effect of on-site carbon production on effluent treatment cost.

The results of this study have shown that it will be hard to produce an activated carbon from hydropyrolysis char at a cost lower than that of most commercial water grade carbons, if one is interested in making no more than

181.6 kg/hr of carbon for use at one location. Carbon production rates greater than 181.6 kg/hr can result in carbons that are lower in cost than commercial grades. But the true reason for this study was to investigate the production of on-site activated carbons for the purpose of lowering effluent treatment costs. This purpose can be accomplished if an on-site production facility with a capacity of 136.2 kg/hr or more of activated carbon is available. This means that the carbon make-up requirements for the equivalent of at least three effluent treatment facilities would have to be produced at the location of one plant.

REFERENCES

1. Timpe, W.G., Lang, E.W., and Miller, R.L. "Kraft Pulping Effluent Treatment and Reuse - State of the Art." EPA-R2-73-164. February 1973.

2. Lang, E.W., Timpe, W.G. and Miller, R.L. "Activated Carbon Treatment of Unbleached Kraft Effluent for Reuse." EPA-660/2-75-004. April 1975.

3. Timpe, W.G., "Pyrolysis of Spent Pulping Liquors." U.S. Patent No. 3,762,989. October 1973.

4. Timpe, W.G., Evers, W.J. "The Hydropyrolysis Recovery Process." Tappi 56 (8): 100. August 1973.

5. Van Krevelen. Coal Science. 1964.

6. Mattson, J.S., and Mark, H.B. Jr. Activated Carbon - Surface Chemistry and Adsorption from Solution. 1971.

7. Torikai, N. and Walker, P.L. Jr. "Activation of Bituminous Coal Lithotypes in Carbon Dioxide," Office of Coal Research November 1968.

8. King, J.G., MacDougall, H., and Gilmour, H. Paper No. 47, Dept. of Scientific and Coal Research, His Majesty's Stationary Office, London. 1930.

9. Lowry, H.H. (Ed). Supplementary Volume - Chemistry of Coal Utilization. 1936

10. Brunauer, Emmett, and Teller. "Adsorption of Gases in Multi-Molecular Layer." Proceedings of American Chemical Society. February 1938.

11. Mandi, S.P., Walker, P.L., and Austin, L.G. Vol. II, Physics and Chemistry of Carbon. 1966.

12. Dubinin, M.M. "The Potential Theory of Adsorption of Gases and Vapors for Adsorbents with Energetically Non-Uniform Surfaces." Chemical Reviews 60: 235-41. 1960.

13. Waeth, H. and Rand, B. Carbon 9. p. 47. 1971.

14. Rigling, J.J. and McEnaney, B. 2nd Conference on Industrial Carbon and Graphite, London. p. 380. 1966.

15. Hutchins, R.A. "Thermal Regeneration Costs." Chemical Engineering Progress 71(5): 80. 1975.

APPENDIX A

ANALYTICAL PROCEDURES

The methods used for analyses of samples in the work covered by this report are listed below. The standard method number given refers to the method in the 13th edition of Standard Methods for Examination of Water and Wastewater, APHA (1971). Methods modified by St. Regis Paper Company are available on request.

TOC and TIC - Std Method 138 using a Beckman 915 total carbon analyzer; sample filtered through Whatman No. 2 paper filter.

pH - Std Method 144A.

Na_2S - Mercuric chloride titration method according to E. Bilberg, Norsk Skogindustri, 11/58 470 (1958), modified by St. Regis Paper Company.

Na_2S and $Na_2S_2O_3$ - by unpublished methods developed by St. Regis Paper Company.

Sulfate - Std Method 156B, gravimetric method.

Metal ions - Std Method 129A using atomic adsorption with Perkin-Elmer Model 403 spectrophotometer.

Volatile Acids - by gas chromatographic method of S. M. Aronovic, et al, Tappi 54, 1963 (1971) and modified by St. Regis Paper Company.

Total Solids - Microwave drying method according to Kemeny & Chazin Tappi 56, No. 8, 81 (1973). Modified by St. Regis Paper Company.

Sulfur, Carbon and Hydrogen - Rapid combustion method using a Leco induction furnace. Method modified by St. Regis Paper Company.

pH Titration - Method developed by St. Regis Paper Company' using a Sargent recording titrator.

Density - Calibrated pycnometer method. TAPPI Standard T625ts-63.

Volatile Matter and Ash - ASTM D271.

Nitrogen Surface Area - Brunauer, Emmett, and Teller. "Adsorption of Gases in Multi-Molecular Layers." Proceedings of American Chemical Society, February 1938.

Carbon Dioxide Surface Area - Dubinin, M. M. "The Potential Theory of Adsorption of Gases and Vapors for Adsorbents with Energetically Non-Uniform Surfaces." Chemical Reviews 60: 235-241 1960.